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REMOVAL OF TRACE QUANTITIES OF

NEPTUNIUM & PLUTONIUM FLUORIDES FROM

URANIUM HEXAFLUORIDE

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P-28
¼ of Np occured in UF₃ fed to cascade to cascade
of total Pu "   "   only a trace fed to UF₆
order of stability of TRU hexafluorides in UF₆

A B S T R A C T

A fixed bed oxidation-reduction system has been
developed to remove parts per million quantities
of neptunium and plutonium hexafluorides from
uranium hexafluoride. The process, which has
been demonstrated on a laboratory scale, utilizes
selective reduction of neptunium and plutonium
hexafluorides on a bed of cobaltous fluoride pel-
lets and allows the uranium hexafluoride to pass
through the trap unchanged. If desired, regenera-
tion of a loaded trap may be accomplished by fluor-
ination of the pellets to recover the transuranic
elements as hexafluorides followed by hydrogen
reduction to again form cobaltous fluoride.

In conjunction with the trapping process, a sampl-
ing procedure has been developed which is adequate
for field sampling uranium hexafluoride cylinders
for that portion of the transuranic hexafluorides
which could be volatilized from the cylinder.

Table of Contents

LIST OF TABLES

LIST OF FIGURES

REMOVAL OF TRACE QUANTITIES OF
NEPTUNIUM & PLUTONIUM FLUORIDES FROM
URANIUM HEXAFLUORIDE

INTRODUCTION

All existing commercial U. S. power reactors utilize uranium enriched in the ^{235}U isotope as a fuel. The nuclear reaction chiefly results in the production of fission products which form during fuel burnup, but significant amounts of transuranic elements are also formed by the capture of neutrons by uranium atoms. Reprocessing of irradiated nuclear fuels from light water reactors by the solvent extraction process effectively separates the uranium, but traces of neptunium, plutonium, and fission products remain with the uranium. Plutonium is then recovered and the uranium is available for recycle to enrichment plants. Very small quantities of neptunium and plutonium accompany the uranium through the process and may be ultimately deposited in uranium conversion facilities, UF_6 shipping cylinders, and in enrichment plants.

The specification for transuranic elements in diffusion plant UF_6 feed was developed in the mid-1960's by considering then available separation technologies, the expected feed rate, the properties of chemical compounds involved, and the distribution of the materials in the feeding process and in enrichment plants. A final consideration was the permissible equipment contamination that could be tolerated and still permit equipment maintenance to be performed in a safe and economical manner. The current specification value, 1500 α dpm/gU (established in 1967), was based on the feed rates expected up to 1975. On a weight basis, this limits the ^{237}Np to about one part per million or the ^{239}Pu to 0.01 part per million. This specification value represented an "as low as practical" limit in the 1967 period. If the "as low as practical" rule were followed today, this specification could be reduced substantially based on current technology and, indeed, ERDA has the matter under consideration. The technology that makes a reduction in this specification limit possible is discussed in this paper.

With this background, two problems were to be resolved by this study. First, it was necessary to develop a sampling method that would permit an accurate estimation of the amount of transuranics being fed to the cascade at the low levels required. Secondly, a method was desired to accomplish a reduction in concentration of transuranics beyond that obtained in the solvent extraction step of the fuel reprocessing cycle.

Some fifteen or more years ago the Paducah Plant started processing production reactor return uranium to UF_6 and feeding it to the diffusion plant. This reactor material contained small quantities of neptunium and plutonium, and both elements have been found in diffusion plant deposits. The chemical reactivity of the hexafluorides of

interest is in the order $PuF_6>NpF_6>UF_6$. Plutonium hexafluoride is
considerably more reactive and more easily reduced to the nonvolatile
tetravalent state than is neptunium hexafluoride. The greater stabil-
ity of NpF_6 results in it being more easily transferred along with the
UF_6 during vaporization. Both neptunium and plutonium have been found
in cascade equipment, and as expected, neptunium is present in larger
amounts. It is anticipated that any procedure which effectively re-
moves the neptunium will also be adequate for removal of plutonium.

A trapping process was developed that achieved a decontamination factor
of 200 to 400 for neptunium and 10,000 to 100,000 for plutonium. The
trapping material is cobaltous fluoride (CoF_2) which operates by re-
ducing the volatile hexavalent transuranic fluorides to the nonvolatile
quadravalent fluorides. The cobaltous fluoride, while somewhat ex-
pensive, is available commercially, is inert to UF_6, and can readily
be handled and converted to a usable granular material that is suitable
for large-scale use. This report describes the development of the
cobaltous fluoride trap including the methods used to prepare the gran-
ular trapping material. The sampling studies and experimental details
are described in the appendix.

EXPERIMENTAL

Previous experience with purification of UF_6 suggested that the most
straightforward decontamination procedure seemed to be to develop a
trapping procedure which would remove the traces of neptunium and plu-
tonium without affecting the UF_6. The task then became simply to find
a material that would accomplish the desired goal. In addition, the
trapping material should be available at a reasonable price, must be
capable of being formed into a suitable shape for contacting the UF_6,
and must have suitable properties to permit handling without requiring
unusual procedures.

There are two trapping mechanisms which could possibly be useful: the
material could adsorb or complex the neptunium and plutonium, or the
material could react to change the chemical form of the neptunium and
plutonium. At the same time, the material must be inert toward UF_6.
This inertness requirement severely limits the number of possible mate-
rials. As a first approximation, one can consider only inorganic com-
pounds, and these would be largely limited to fluorides.

Scoping Tests

A laboratory system was fabricated to allow simultaneous scoping tests
on several metallic fluorides. The fluorides of Ba, Ca, K, Li, Mg, Na,
Sr, Ni, Cu, and U(IV) were exposed to 152 mm of static NpF_6 vapor at
various temperatures from 95° to 400°C for 115 hours. The fluorides,
about 100 mg of each, were placed in micro nickel boats in a 1-inch
reaction chamber, dried by exposure to fluorine at 150°C for 24 hours,
and evacuated at 315°C to remove the HF formed during drying. The dry-
ing of UF_4 was accomplished without the use of fluorine by evacuating
at 150°C. The reactor temperature was then adjusted to the desired
value and NpF_6 vapor admitted. During the test, the NpF_6 was removed
periodically and a fresh charge admitted. Following the exposure, the
entire sample was dissolved in 6 $\underline{N}$ $HNO_3 \cdot 0.1$ $\underline{M}$ $Al(NO_3)_3$ for analysis.
Table 1 summarizes the results.

Table 1

SORPTION OF NpF₆ BY METAL FLUORIDES

Material	Surface Area M^2/g	Neptunium Absorbed, % (g Np/g metal fluoride)x 100			
		95°C	150°C	260°C	400°C
	*Initial NpF₆ Pres., mm	152	152	152	152
LiF	3.0	–	1.1	0.47	3.1
NaF	0.6	–	102	177	162
KF	0.1	–	21.8	172	258
MgF₂	116	–	5.5	5.8	1.7
CaF₂	20.7	–	2.0	3.2	18.4
SrF₂	25.7	–	1.8	5.7	9.5
BaF₂	2.3	–	0.4	10.5	39.1
NiF₂	39.5	–	1.4	–	–
CuF₂	2.2	–	0.02	–	–
AlF₃	85.5	–	1.0	–	–
UF₄	0.9	8.1	–	–	–

*Pressure varied from 152 mm to 10 mm during
exposure due to consumption and/or reduction
of NpF₆.

An evaluation of the data from the scoping runs indicated that four of
the fluorides, NaF, KF, BaF₂, and MgF₂, were possible candidates. Po-
tassium fluoride trapped the most neptunium, but the extreme hydroscopic
nature of this compound would introduce difficulty if used on a plant
scale. Likewise, NaF is undesirable due to the fact that it complexes
with UF₆ at bed temperatures below 409°C. UF₄, which also showed some
sorption, is not inert to UF₆. In view of this, MgF₂ and BaF₂ were
chosen for testing in a dynamic sorption system.

For the dynamic tests, small pellets were prepared and a trap 7/8-inch
in diameter by 1-foot long was constructed. The pellets were prepared
using water for agglomeration on a rotating disk pelletizer following
the procedure of Richardson and McNeese.[1] The physical properties of
the pellets before drying are shown in table 2. Prior to use, the
pellets were dried with fluorine at about 150°C.

[1]Richardson, E. W., and McNeese, L. E., United States Patent
No. 3,372,004, March 5, 1968.

Table 2

PROPERTIES OF METAL FLUORIDE PELLETS

	MgF_2	BaF_2
Mesh Size	-8, +12	-8, +10
Surface Area, M^2/g	130	0.3
Void Fraction	0.35	0.56
Moisture, % (before drying)	10.2	0.04

The materials were tested by passing a stream of UF_6 containing 90-140 ppm NpF_6 through the traps. Neither trap was particularly effective with the MgF_2 trap reducing the neptunium concentration from 142 to 26 ppm while the BaF_2 unit reduced the concentration only from 89 to 83 ppm. Other details of the runs are given in table 3.

Reduction Studies

While the MgF_2 showed some promise, it did not achieve the desired decontamination. Attention was next directed toward materials that might react with the transuranic fluorides. The actinide hexafluorides are produced with increasing difficulty as one proceeds through the series U, Np, and Pu. Although all of these hexafluorides are considered very reactive, differences do exist in their relative stabilities. This information suggested that by carefully choosing a reactant and conditions one could selectively reduce a less stable hexafluoride in the presence of one which is more stable.

Application of this reasoning led to a search for a material which would preferentially reduce NpF_6 and PuF_6 to the tetravalent state yet not react with UF_6. Free energy calculations indicated that certain lower valent fluorides such as FeF_2, AgF, CoF_2, and PdF_2 were promising materials. Due to economic considerations and availability of the metal fluorides, FeF_2 and CoF_2 were chosen for initial testing. The FeF_2 was quickly eliminated from consideration when the initial tests showed that it reduced UF_6 and CoF_2 did not.

Cobaltous fluoride powder was obtained from the Harshaw Chemical Company and was pelletized in the same manner as the BaF_2 and MgF_2. However, the finished pellets had insufficient physical strength for use. Since CoF_2 is somewhat soluble in water, tests were conducted to determine the effect of adding an excess of water during or after the pelletizing process. Simultaneous experiments were conducted to study the effect of sintering the CoF_2 pellets. It was determined that CoF_2 pellets exhibiting poor physical strength could be sintered at about 650°C in an anhydrous HF atmosphere to impart the desired physical strength. It was determined also that CoF_2 powder pelletized in the normal manner followed by "wetting" the finished pellets with a water spray resulted in pellets possessing the necessary physical strength. This procedure was used rather than sintering.

Table 3

NpF$_6$ TRAPPING STUDIES BY SORPTION

	MgF$_2$	BaF$_2$
Operating Conditions		
Weight in bed, g	107.9	185.2
Temperature, °C	121	121
Superficial velocity, ft/sec	1.30	0.65
Av. inlet conc., ppm Np (U basis)	142.0	89.4
Av. outlet conc., ppm Np (U basis)	26.0	83.0
Length of run, hrs	4.5	1.75
Bed Analyses		
First inch from inlet end:		
Np, mg	32	0.41
Np/metal fluoride, mg/g	2.69	0.01
Next two inches:		
Np, mg	34	0.024
Np/metal fluoride, mg/g	1.49	0.0005
Last nine inches:		
Np, mg	136	0.026
Np/metal fluoride, mg/g	1.85	0.0002
Np retained in trap, % of amount fed	48	0.4
Total Np fed, mg	420	111
Total Np in trap, mg	202	0.5

After forming, the pellets contain about 30% water which must be removed prior to use. Thermobalance studies indicated that the water could be reduced to about 1% by heating in nitrogen or HF to 315°C. Above 315°C some deterioration was noted along with a decrease in the surface area. Table 4 gives the results of several drying experiments under different conditions. Chemical analysis of the dried pellets shows negligible deterioration in either nitrogen or HF (theoretical Co is 60.8%), but there was some decrease in surface area in HF. This surface area decrease could be attributed to incomplete HF removal, but the point was not resolved since a nitrogen atmosphere seemed to be quite satisfactory and is obviously simpler and less expensive. An additional confirmation that the nitrogen dried pellets were satisfactory was obtained by an x-ray diffraction analysis which showed that only CoF$_2$ was present. Nitrogen drying was therefore adopted.
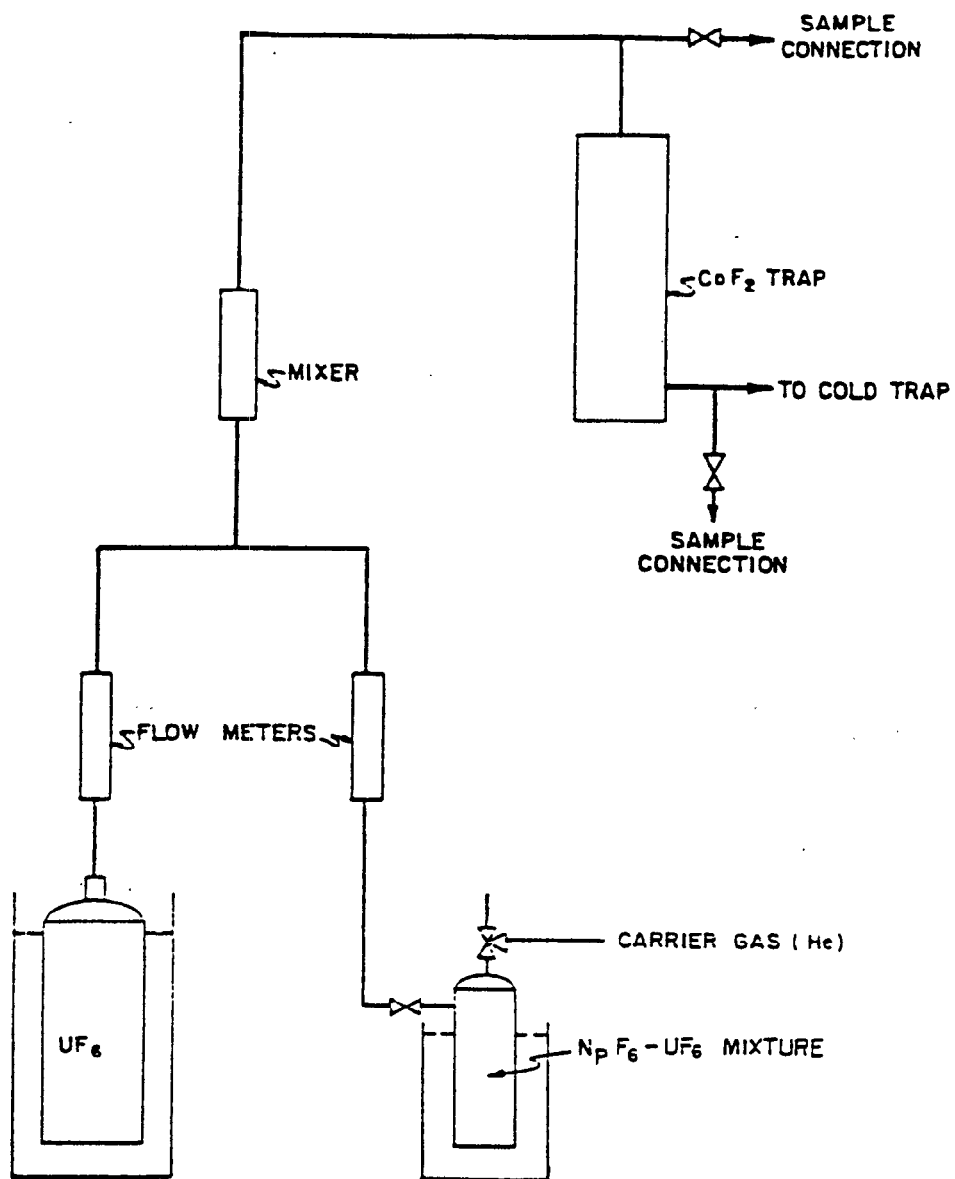
Table 4

RESULTS FROM CoF₂ DRYING EXPERIMENTS

Conditions	Temp., °C	H_2O, %	Co(II), %	F, %	Surface Area, M^2/g
HF Dried	315	1.2*	-	-	-
HF Dried	315	1.4	59.8	38.3	8.2
HF Dried	205	1.8	59.7	38.2	8.7
N₂ Dried	315	1.0	-	-	-
N₂ Dried	315	1.6	60.9	37.4	20.2
N₂ Dried	260	1.7	60.3	37.6	25.4

*Calculated from thermobalance data.

One brief further word about drying. During the course of the drying experiments, it was noted that removal of the 1% residual water can be accomplished by treatment with fluorine at elevated temperature. This oxidizes the CoF₂ to CoF₃ which must then be reduced with hydrogen back to CoF₂. This process was used as an analytical procedure for water and was also used to provide absolutely dry CoF₂ for the one plutonium trapping run. The physical properties of the pellets are not affected by this single cycle of oxidation and reduction.

To test the pellet efficiency, a trap was constructed with dimensions similar to those used in the MgF₂ tests (7/8-in x 12-in.). The test system, shown in figure 1, was designed to provide a continuous supply of UF₆ with a NpF₆ concentration of 10-50 ppm. A metered stream of helium, used as carrier gas, was passed through a storage cylinder containing a UF₆-NpF₆ mixture of known concentration. After saturation of the helium with the UF₆-NpF₆ mixture, it passed into the nickel mixer where it was diluted with a larger stream of UF₆. The mixture was then fed to the CoF₂ trap with hourly sampling of the inlet and outlet gas streams. A UF₆ mass flow of 1.02 kg/hr was used for each run. At the termination of each run, the contents of the trap were analyzed for neptunium and uranium. Conditions for the runs are shown in table 5 and the results of bed analyses are shown in table 6.

The data from the scoping studies indicated that CoF₂ would remove neptunium at 100°C but that a greater trapping efficiency would be realized by operation at the higher temperatures of 150°C and 226°C as shown by the lower outlet concentrations and higher decontamination factors at the higher temperatures. Examination of the bed loading data also shows that the higher temperatures result in more efficient trap operation. To show this more clearly, some of the data from table 6 have been plotted in figure 2. Here the bed loading, as represented by the neptunium concentration in the first inch of bed material, is plotted as a function of temperature. The data, normalized for feed rate, indicate that substantially higher loading is obtained at 150 and 226°C.

SYSTEM FOR TRAPPING STUDIES

FIGURE I

Table 5

NEPTUNIUM SCOPING RUN CONDITIONS

	226°C*		150°C	100°C
	A	B		
Av. Inlet Conc., ppm Np (U basis)	24.40	40.40	28.00	41.50
Av. Outlet Conc., ppm Np (U basis)	0.61	0.58	0.24	1.70
Length of Run, hrs	9.75	5.25	16.00	10.00
Superficial Bed Velocity, ft/sec	0.40	0.40	0.31	0.27
Residence Time, sec	2.5	2.5	3.2	3.7
Decontamination Factor	40	70	117	24

*The same bed material was used in runs A and B.
 The inlet concentration was increased after 9.75 hours.

The conclusion from these scoping studies was that CoF_2 is effective
for removing NpF_6 from a UF_6 vapor stream over a wide temperature range,
and designs incorporating longer retention time at lower temperatures
or vice versa are possible. An empirical evaluation of the scoping
data indicated that 150°C would be most advantageous for additional
laboratory studies.

To define the important operating conditions further, runs were made to
evaluate the effects of bed length, gas flow velocity, bed temperature,
and NpF_6 gas concentration on the retention efficiency of CoF_2 for NpF_6
in a UF_6 vapor stream. The experimental apparatus used for these studies
was the same as before except that a second 4-foot long CoF_2 bed was
added in series with the 1-foot trap. Provisions were made to sample
the gas stream at the inlet to the trap, after one foot of CoF_2, and
at the outlet of the 4-foot trap. The experimental procedure was the
same as for the scoping runs.

The NpF_6 trapping system was operated for 58 hours with an average inlet
concentration of 93.5 ppm Np (U basis) to obtain an initial loading on
the trap. After this period, consecutive experiments evaluated the vari-
ables of inlet concentration, trap temperature, and superficial bed
velocity. Initial operating conditions, except superficial bed velocity
which was increased from 0.29 ft/sec to 0.50 ft/sec, were then resumed
until breakthrough of the 1-foot trap section was indicated. The inlet
concentration was then reduced to approximate actual "clean-up" condi-
tions and additional data obtained. The loading study was terminated
after 226 hours of flowing time, and analyses of material from respec-
tive bed sections were made. A summary of the conditions for the loading
studies and parameter investigations is shown in table 7. Results of
the bed analyses are shown in table 8.

Table 6

BED ANALYSES FROM NEPTUNIUM SCOPING STUDIES

	226°C			150°C			100°C		
	First 1" of CoF$_2$	Next 2" of CoF$_2$	Last 9" of CoF$_2$	First 1" of CoF$_2$	Next 2" of CoF$_2$	Last 9" of CoF$_2$	First 1" of CoF$_2$	Next 2" of CoF$_2$	Last 9" of CoF$_2$
Total Np, mg	360	67.0	62.6	136	147	171	143	53.7	125
Np/CoF$_2$, mg/g	48.0	6.0	1.26	22.2	15.1	3.31	14.5	4.07	2.59
*Total Np Trapped, mg	497.8			460.3			327.7		
Total Np Fed, mg	560.0			411.0			315.0		
Np Recovered, %	89			112			104		

*Includes neptunium found in bed analysis plus neptunium found in trap wash.
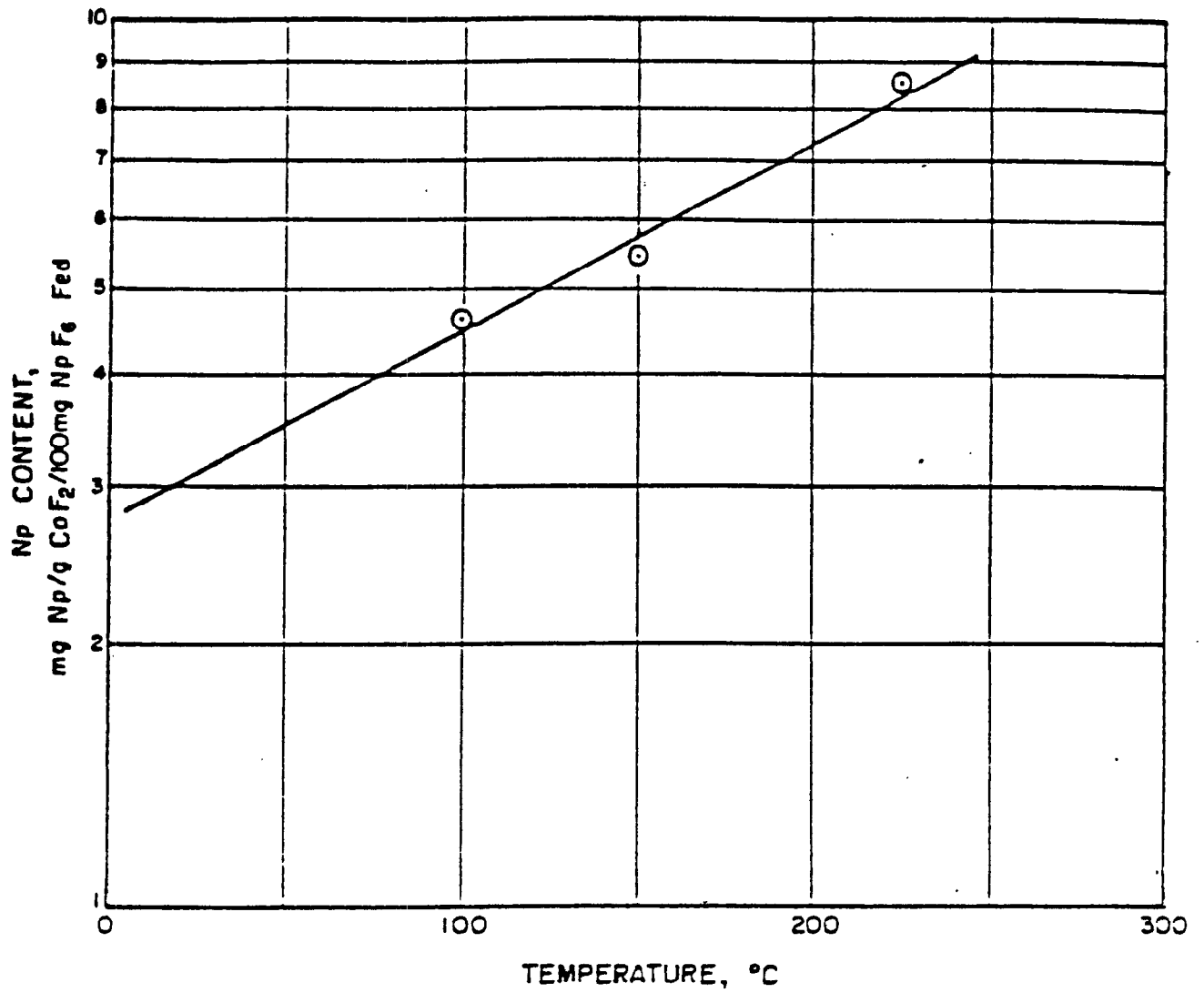
NEPTUNIUM CONTENT OF FIRST INCH OF BED

FIGURE 2

Table 7

OPERATING CONDITIONS FOR CoF_2 LOADING STUDIES

Flowing time, hrs	58	20	22	34	14	38[1]/	28
Temperature, °C	150	150	226	150	150	150	150
Pressure, psia	14.7	14.7	14.7	14.7	14.7	14.7	14.7
Superficial velocity, ft/sec	0.29	0.25	0.25	0.50	1.0	0.50	0.50
Residence time, sec	17.2	20.0	20.0	10.0	5.0	10.0	10.0
Av. inlet-1 conc., ppm Np (U basis)[2]	93.5	17.0	9.8	9.0	13.3	106	23.4
Av. outlet-1 conc., ppm Np (U basis)[3]	6.1[6]/	0.67	0.18	0.58	1.07	47.6	8.0
Av. outlet-2 conc., ppm Np (U basis)[4]	0.12	0.08	0.05	0.04	0.03	0.40	0.03
Decontamination Factors							
First foot	15	25	54	16	12	–	–
Last 4 feet	51	(8)[5]/	(4)[5]/	(15)[5]/	(36)[5]/	119	160
Overall	780	210	200	230	440	270	780

[1] Breakthrough occurred in the 1-foot trap during this period.
[2] Inlet concentration to the CoF_2 trap.
[3] Outlet concentration after the 1-foot trap.
[4] Outlet concentration after the 4-foot trap.
[5] Values probably low because of low inlet concentration.
[6] Believed to be contaminated.

Table 8

BED ANALYSES FROM NpF$_6$ TRAPPING RUN

Sample Origin	No Found			U Conc., %
	g	%*	Cumula-tive, %**	
First inch of CoF$_2$ from inlet end	0.74	10.2	6.4	1.8
Next 2 inches	1.56	11.8	20.0	2.2
Next 9 inches	4.55	7.3	59.6	7.5
Next foot	2.26	3.3	79.2	9.1
Next foot	1.11	1.6	88.9	12.7
Next foot	0.62	0.8	94.3	13.8
Next foot	0.16	0.2	95.7	14.3

*Based on amount found.
**Based on amount fed.

In evaluating the data obtained in the investigation of the process parameters, it was concluded that trapping efficiency does depend to a degree on inlet concentration. Reducing the inlet concentration from 93 to 17 ppm Np (U basis) had little significant effect on the trapping efficiency of the 1-foot section, but the overall decontamination factor for the 5-foot trap dropped from 780 to 210 and the outlet neptunium concentration dropped from 0.12 to 0.08 ppm. Increasing the temperature from 150°C to 226°C resulted in a slight improvement in trapping efficiency only for the 1-foot section. The difference between 0.25, 0.50, and 1.0 ft/sec superficial bed velocity was negligible for the 5-foot section and had only a slight effect on the 1-foot section.

At the termination of the loading studies, 11.5 g of neptunium had been fed to the system. Based on the bed analyses, table 8, ~60% of the neptunium was retained in the first foot. Overall, 95.7% of the neptunium fed was accounted for in the bed. It is believed that the slightly low recovery percentage was caused by some of the particulate NpF$_4$ which had been retained on the CoF$_2$ pellet surface becoming entrained in the UF$_6$ gas stream. A portion of this would be deposited throughout the length of the trap with a small percentage passing out the outlet of the trap. The gas samples were taken through sintered metal filters which precluded any indication of such occurrence. This theory is supported by the data which shows that the first inch of CoF$_2$ contained less neptunium than the next 2-inch section. A filter at the trap exit could easily eliminate the solid carryover. Figure 3 illustrates the distribution of neptunium throughout the trap.
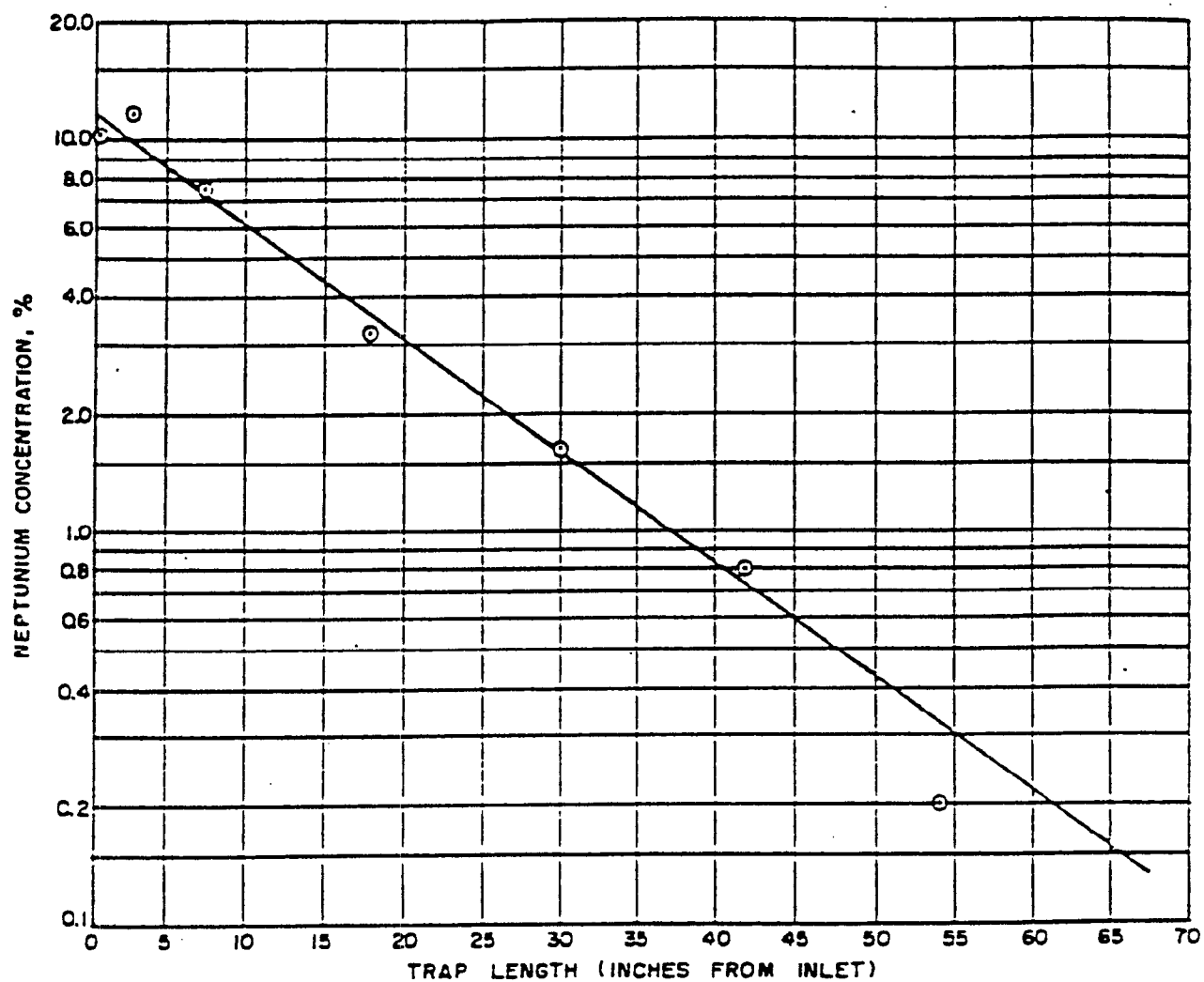
DISTRIBUTION OF Np IN CoF$_2$ TRAP

FIGURE 3

The CoF_2 bed material underwent a color change from pink to shades of brown upon exposure to NpF_6. The brownish color was more distinct in the first few inches, decreasing in intensity progressively from inlet to outlet as the CoF_2 was converted to CoF_3. Analyses of the bed material by x-ray diffraction after exposure to NpF_6 confirmed the presence of NpF_4. Valence analysis of the neptunium indicated that all of the neptunium present was in the tetravalent state. These data confirm that the trapping system operates as an oxidation-reduction system as shown in equation 1.

$$NpF_6 + 2CoF_2 \rightarrow NpF_4 + 2CoF_3 \tag{1}$$
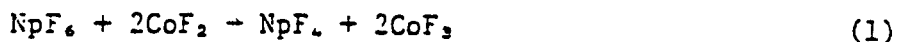
Considering the overall 5-foot length of the trap, an average decontamination factor of 370 was obtained before breakthrough occurred in the first one-foot section and for the complete run an average decontamination factor of 416 was observed. The decontamination factors given in table 7 are plotted as a function of trap length and shown in figure 4. Only data where the inlet neptunium concentrations were in the range of 5-100 ppm were used to construct the graph since the decontamination factor appears to be somewhat a function of gas concentration. These data indicate that decontamination factors of 600 can be achieved with a trap length of 6 to 7 feet which is a quite feasible trap length.

It is concluded that a practical method has been developed for the selective removal of neptunium from a UF_6-NpF_6 stream containing up to about 100 ppm Np (U basis) (156,000 α dpm/gU). A loading factor in excess of 3% of the bed weight can be obtained with a single trap. Gas velocities up to 1.0 ft/sec are satisfactory at a bed temperature of 150°C.

It should be noted that the loading data presented here do not represent a CoF_2 trap loaded to the maximum concentration of neptunium. Because of the time element and the amount of neptunium that would be required to reach maximum concentration, the goal was to operate the system only to the extent of attaining a breakthrough in the 1-foot section. At the termination of the run, this goal had been reached although a decontamination factor of 2 was still evident for the 1-foot section. Obviously, the loading factor of 3% of the bed weight is a conservative figure.

To generate trap design criteria, an experiment was conducted to determine the pressure drop of a packed CoF_2 sorption trap. A trap 5-feet long by 1-inch in diameter was packed with CoF_2 pellets and mounted vertically. Nitrogen was passed through the trap at 22°C and 14 psia. The pressure difference between inlet and outlet at various gas velocities was determined. The data are shown in figure 5.

While PuF_6 should be more easily reduced than NpF_6, a run similar to the last neptunium run was made to develop operating parameters for plutonium removal. The same system, using only the 1-foot long trap, was used. The effects of plutonium concentration, reaction temperature, and gas velocity were investigated.

FIGURE 4

NEPTUNIUM
DECONTAMINATION FACTOR
VS
TRAP LENGTH

SUPERFICIAL GAS VELOCITY, Ft/Sec
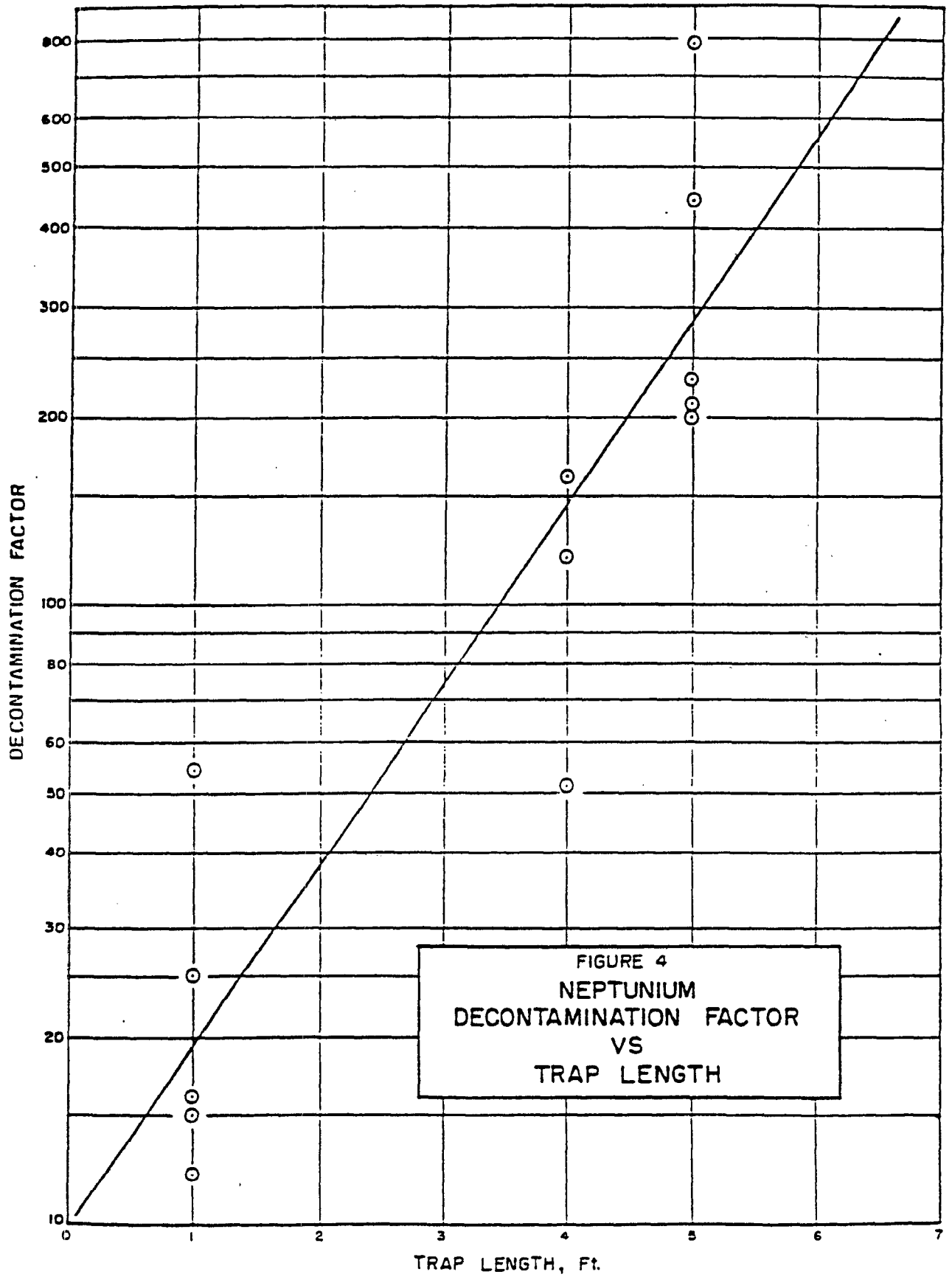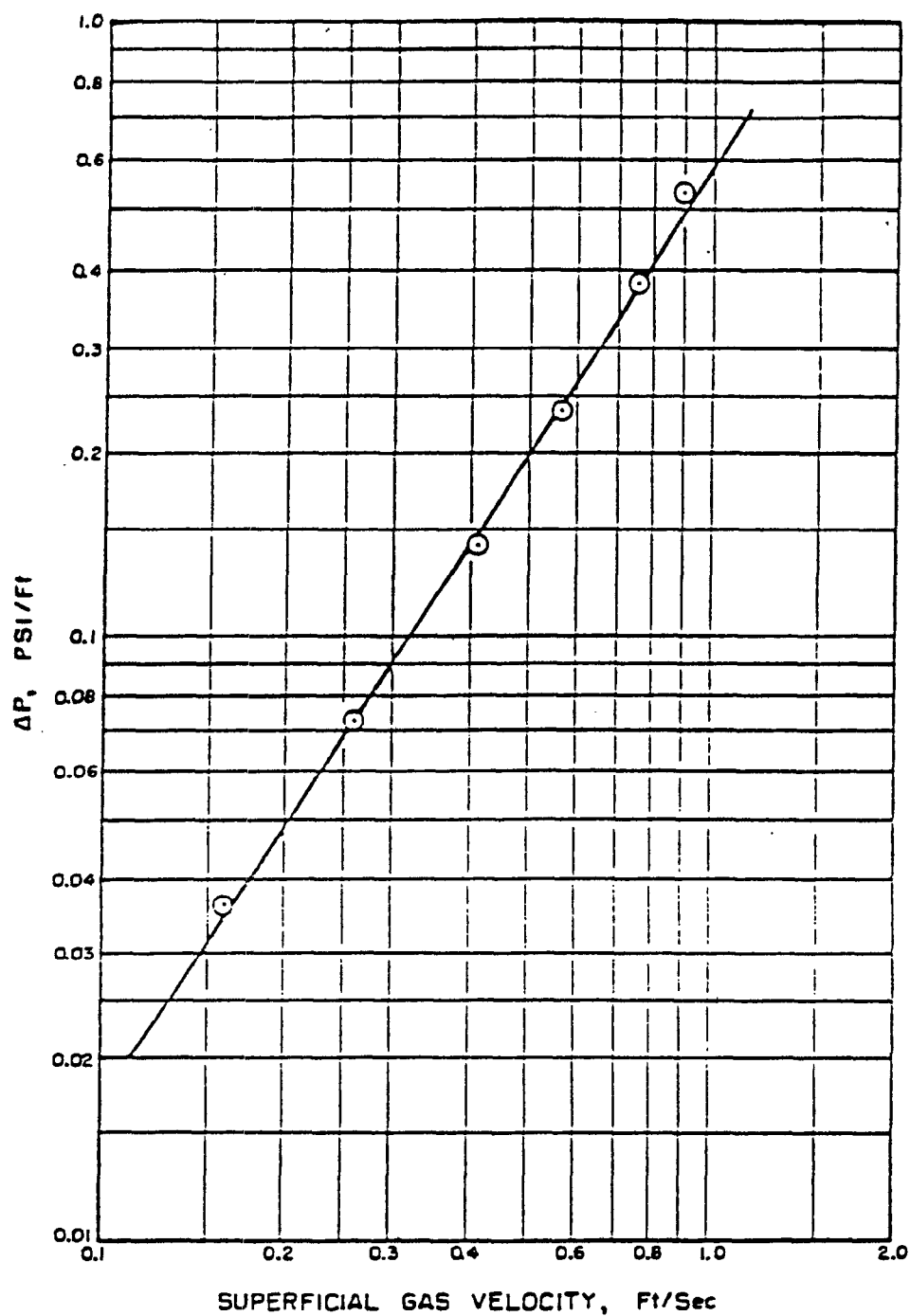
NITROGEN PRESSURE DROP ACROSS CoF$_2$ TRAP

FIGURE 5

In previous neptunium removal studies, it was observed that approximately 10% of the bed weight was composed of uranium at the termination of the run. This was due to the reaction of UF_6 with residual water in the pellets. Uranium retention would not be of serious consequence in the field decontamination of depleted uranium but would be undesirable when using enriched uranium. One of the objectives of the plutonium removal studies was to investigate uranium retention on a dry CoF_2 bed. Since it was previously determined that CoF_2 pellets could not be completely dried using either HF or nitrogen, the pellets were subjected to a fluorine oxidation – hydrogen reduction cycle to ensure complete dryness. The loaded 1-foot long trap was dried in nitrogen at 260°C and then treated with fluorine at 230°C followed by hydrogen at 260°C.

The run summarized in table 9 was conducted as before. After 52 hours the plutonium concentration was raised from 700 ppb to 8,000 ppb and, while still at a high concentration, the trap temperature was reduced from 150 to 100°C. Finally, the gas velocity was increased to 1 ft/sec, four times the previous velocity. As was expected, plutonium was easily reduced by the trap and, even though only a 1-foot trap was used, decontamination factors near 100,000 were obtained for most of the runs. None of the changed operating conditions significantly affected the trap performance. It is concluded that the trap can be operated under a wide variety of conditions of temperature, flow, and plutonium concentration and still effectively provide satisfactory plutonium decontamination.

Table 9

PuF$_6$ REMOVAL STUDIES

Phase	1	2	3	4
Flow time, hrs	52	24	24	18
Superficial gas velocity, ft/sec	0.25	0.25	0.25	1.0
Pressure, psia	14.7	14.7	14.7	14.7
Trap temperature, °C	150	150	100	150
Residence time, sec	4.0	4.0	4.0	1.0
Av. inlet, ppb Pu (U basis)	700	7993	5747	889
Av. outlet, ppb Pu (U basis)	0.08	0.06	0.05	0.01
Decontamination Factor	8.8×10^3	1.3×10^5	1.1×10^5	8.9×10^4

At the termination of the removal studies, the CoF_2 trap was emptied. Approximately one-half of the pellets from the first inch adjacent to

the trap inlet were light brown in color, characteristic of CoF$_3$. It appeared that most of the PuF$_4$ had been reduced in this bed section. The pellets still possessed good physical strength. Samples of the bed material were analyzed for total plutonium, total uranium, and for cobalt and plutonium valences. Analytical data are shown in table 10.

Table 10

URANIUM AND VALENCE ANALYSES FOR CoF$_2$ BED MATERIAL

	First Inch from Inlet, wt.%	Next 2", wt.%	Next 3", wt.%	Last 6", wt.%
Co (III)	6.6	-	-	-
Co (II)	33.5	-	-	-
Pu (IV)	4.2	-	-	-
Pu (III)	2.3	-	-	-
Pu (VI)	<0.2	-	-	-
U	4.1	1.1	1.4	0.1

These data indicate that the reaction between PuF$_6$ and CoF$_2$ is not exactly analogous to that of NpF$_6$ but that some of the PuF$_6$ is being reduced to the trivalent state. This presents no problem since PuF$_3$ is nonvolatile and the retention mechanism would be the same as for PuF$_4$. A total of 1.1 wt.% U was found in the bed material. This is significantly lower than the 5-10% normally found in similar runs where only nitrogen or HF drying was employed, confirming that most of the uranium retention was caused by reaction of UF$_6$ with residual water in the pellet bed.

An overall bed loading of 1.2% was obtained. However, the first inch contained 7.1 wt.% Pu. It is believed that even the 7.1 wt.% Pu is a very conservative value and that a bed loading in excess of that value could be obtained. Finally, it is concluded that a system designed to remove NpF$_6$ would more than adequately remove the PuF$_6$.

Neptunium and Plutonium Recovery

Physical observations of the CoF$_2$ bed material indicated that insignificant deterioration of the pellets occurred during the trapping run. The physical strength of the pellets was sufficient for reuse if the neptunium and plutonium could be removed.

Experiments were conducted to investigate methods of recovering neptunium and plutonium from a loaded trap and recovering the CoF$_2$ for reuse. During the trapping operation, part of the CoF$_2$ is oxidized to CoF$_3$. Since

CoF$_3$ decomposes to a hydroxide when treated with water, aqueous recovery schemes are undesirable. A dry fluorination scheme seemed feasible, and this was investigated and shown to be possible. The procedure consists of reacting the NpF$_4$ and PuF$_4$ with elemental fluorine to reform the volatile hexafluorides which can be collected in a series of cold traps. It was determined that at a reaction temperature of 370°C, the neptunium and plutonium can be effectively removed to a level <0.4 wt.% Pu and ~0.1 wt.% Np. The CoF$_3$ can then be reduced back to CoF$_2$ using hydrogen at 260°C and the pellets reused.

It was previously noted that above 315°C some deterioration of the pellets occurred. This was observed in the drying studies with the wet pellets. In these recovery tests the pellets were completely dry initially, and no dusting or other deterioration was noted.

These data indicate that the loaded bed can be regenerated if necessary or desirable. If this clean-up procedure were to be conducted on a large scale, the hazards involved in handling relatively pure NpF$_6$ and PuF$_6$ must be carefully considered. In addition, very efficient cold traps or other devices must be used to collect the evolved hexafluorides for recovery or disposal. While the economics have not been fully defined, it is suggested that a loaded trap contains the transuranic fluorides in a fixed solid form which should be suitable for long-term radioactive waste storage. Discard of a filled trap should be given serious consideration.

Impurity Removal from Liquid UF$_6$

Utilization of the CoF$_2$ trapping system as a gas phase operation could require modification of the normal flow sheet of the nuclear fuel reprocessing cycle to include a vaporization step. If, however, this process could be extended to include the purification of liquid UF$_6$, then it would have greater versatility.

Scoping studies were conducted to determine if CoF$_2$ would efficiently remove the transuranic impurities from liquid UF$_6$. A schematic diagram of the system which was used is shown in figure 6. A UF$_6$-NpF$_6$ mixture containing approximately 250 ppm Np (U basis) was prepared in a specially modified and fluorine conditioned type 5A cylinder. The mixture was heated to 100°C and drained, in the liquid phase, through a nickel trap (0.43 in. by 24 in. long) containing approximately 30 grams of CoF$_2$ pellets. In the initial test the system was operated for three hours with a mass flow rate of 1.2 kg UF$_6$/hr. In a second test a larger trap (3 in.I.D. by 24 in. long) was used to provide a greater residence time. The trap was filled with CoF$_2$, and the pellets were oxidized and reduced to ensure complete dryness. The trap was then filled with liquid UF$_6$. The UF$_6$ was left in the trap for six hours at 100°C and then drained. Inlet samples were taken while filling the trap and outlet samples removed while draining the trap. A significantly higher decontamination factor was obtained for the second test, due undoubtedly to the longer residence time. Operational and analytical data for the two tests are shown in table 11.
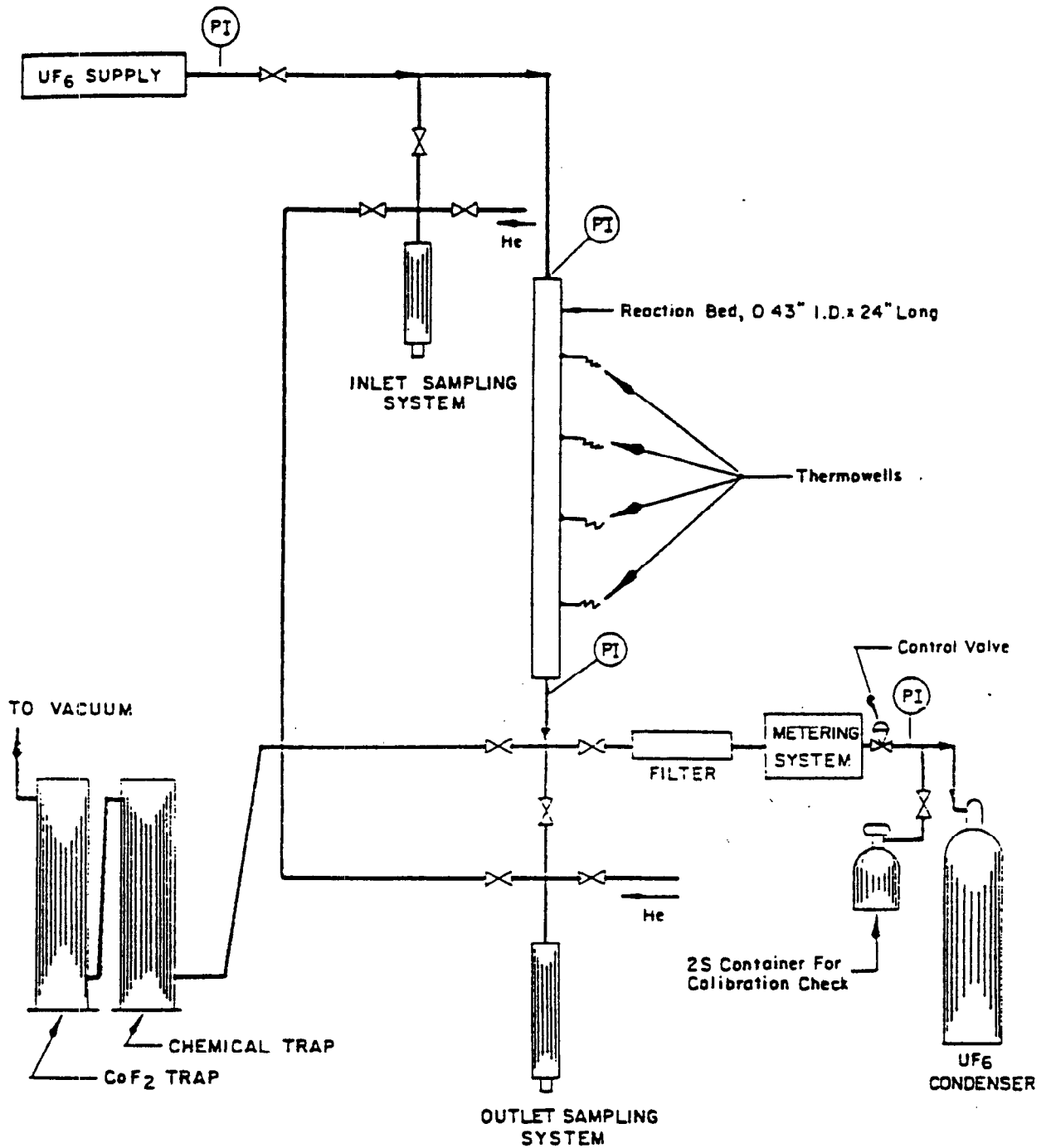
LIQUID UF₆ PURIFICATION SYSTEM

FIGURE 6

Table 11

DATA FOR LIQUID PURIFICATION SYSTEM

	Test 1	Test 2
Trap temperature, °C	100	100
Superficial velocity, ft/sec	0.003	0
Residence time, min	11	360
Mass flow, kg UF_6/hr	1.2	-
Av. inlet, ppm Np (U basis)	222	48
Av. outlet, ppm Np (U basis)	133	0.48
Av. decontamination factor	1.7	100

A field system designed to process 1,000 lbs of liquid UF_6/hr and provide an equivalent residence time would require a trap 22 inches in diameter and 19 feet in length. The physical size of the trap required and the low processing rate combined with the low decontamination factors observed make this system very unattractive. It is concluded that while the liquid purification system using CoF_2 might be useful for some specialized application it would not be feasible for the routine purification of liquid UF_6.

Two additional factors should be emphasized in the use of the CoF_2 reduction system. The cobalt fluoride trap should contain a sintered metal filter in the trap outlet section of approximately 2 micron size. This filter is important to remove fine solid material from the gas stream such as neptunium and plutonium tetrafluorides which are formed in the trap. Use of the trap should also be limited to UF_6 streams which do not contain fluorine or other oxidizing agents which could preferentially oxidize the CoF_2 to CoF_3 and thereby reduce the trap capacity.

CONCLUSIONS

A process has been developed and demonstrated on a laboratory scale to selectively remove trace quantities of neptunium and plutonium hexafluorides from a gaseous mixture with uranium hexafluoride. The process uses a fixed bed of cobaltous fluoride pellets through which the contaminated UF_6 is passed. Neptunium and plutonium hexafluorides are converted to nonvolatile tetrafluorides by reaction with cobalt difluoride and are retained in the pellet trap by a sintered metal filter at the exit end.

At inlet concentrations up to 100 ppm (U basis) decontamination factors of 200 to 400 were obtained for neptunium and of approximately 100,000

for plutonium. Nominal operating conditions for the process are 150°C
at a gas velocity of 1 ft/sec. This process should not be used when the
gas stream contains free fluorine, and it is considered to be practical
only for a gas phase operation.

Studies related to liquid phase sampling of UF₆ contaminated with nep-
tunium and plutonium have led to the conclusion that such samples should
be taken through a fine sintered metal filter. This procedure will re-
move particulate matter and result in a more homogeneous sample. Samples
taken in this manner will not represent the total transuranic content in
a cylinder but will provide a better estimate of the amount of trans-
uranic hexafluorides which could be vaporized out of a cylinder into
the diffusion plants.

ACKNOWLEDGMENT

Appendix A

SAMPLING CONSIDERATIONS

The present specifications for UF_6 to be used for diffusion plant feed require the activity from transuranic elements, which for all practical purposes are limited to neptunium and plutonium, to be not more than 1500 disintegrations per minute per gram of uranium. It is further specified that all analyses shall be performed on liquid samples. As noted earlier, it is the intent of these specifications to keep the diffusion plants from being contaminated by these very toxic materials which would enormously complicate operational and maintenance procedures.

Any process to produce UF_6 would be expected to convert the transuranic elements also to the hexafluorides. Both plutonium and neptunium hexafluoride are reasonably stable at normal UF_6 handling temperatures with plutonium hexafluoride being less stable than neptunium hexafluoride. Because of chemical reactivity, thermal decomposition, and in the case of plutonium also the decomposition due to alpha radiation, the hexafluorides tend to form mixtures of hexafluorides and tetrafluorides. By analogy with uranium, the hexafluorides were assumed to be soluble in UF_6 and the tetrafluorides to be insoluble. Both of these assumptions were ultimately confirmed by actual data. Since the tetrafluorides are not volatile, they would remain in the UF_6 feed cylinder while the transuranic hexafluorides should be vaporized into the diffusion plant along with the UF_6. Plant data indicates that approximately one-fourth of the neptunium originally received in UO_3 was fed to the diffusion plant. Of the total plutonium received, only a trace was ever found to be present in plant equipment. These data support the relative order of stability of the two transuranic hexafluorides in UF_6.

In the past UF_6 cylinders have been liquid sampled for transuranic analyses in the same manner as for other impurities. It is recognized that these samples were taken from a nonhomogeneous system and gave only an indication of the level of transuranics present. Data obtained in this manner did not represent either the total quantity of neptunium or plutonium in the cylinder or the amounts which could be vaporized into the cascade. For these reasons, it was concluded that the best approach would be to filter the liquid sample at the time the sample was taken. Thus, only the soluble hexafluorides would be measured, and it is these materials which would be expected to be vapor transferred to the diffusion plants.

In the following sections of this appendix, a number of experiments are described relating to the preparation and handling of the transuranic fluorides and the development of a system and procedure for obtaining the necessary samples. These techniques were utilized in the development of the CoF_2 trapping system where it was found to be

possible to obtain accurate results even though all transuranic con-
centrations were in the parts-per-million or parts-per-billion range.
As will be pointed out in the following section, operating at these
low levels did result in some stability problems and contamination
was very difficult to control. A number of the initial experiments
were devoted to developing the techniques necessary for coping with
these problems. Generally, data from these early tests have been
omitted from the tabulations.

Appendix B

MATERIALS AND EQUIPMENT

In recognition of the toxicity of the transuranic elements, all experiments where significant quantities of neptunium and plutonium were used were conducted inside a glove box. The box, of the CENHAM type, was similar to that of glove boxes in use at Argonne National Laboratory. The box was nominally 13-ft. long, 8-ft. high, and 3-ft. deep. It was of modular construction, 2-1/2 tiers high by 4 wide, and contained 80 glove ports. Each module contained 8 glove ports, 4 on each side. A photograph of the box is shown in figure B-1.
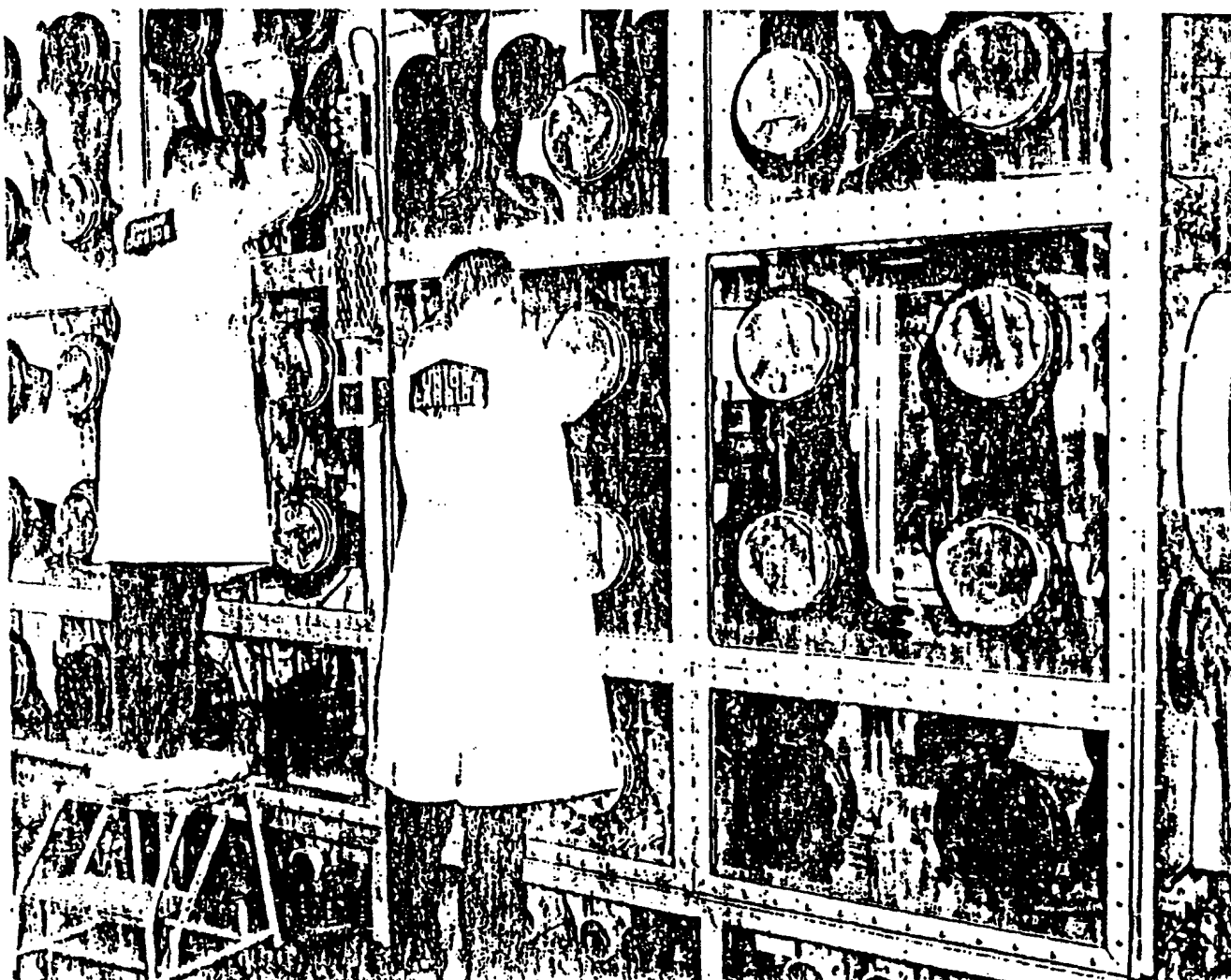
Equipment installed in the box consisted of two separate fluorination reactors with associated furnaces, manifolds, and cold traps. Other necessary apparatus was included for the preparation of NpF_6 and PuF_6, spiking UF_6 with these materials, sampling and hydrolysis of the resulting mixtures, vaporization studies, and sorption and trapping experiments. Facilities for heating and cooling cylinders, vacuum systems with chemical traps, and temperature measuring equipment were also provided. A schematic diagram of the fluorination system and gas pipette system is shown in figure B-2. All operations involving the volatile transuranic compounds were confined to manifolds, reactors, and traps constructed of nickel. Hoke Type 413* Monel valves with Inconel diaphragms were used exclusively.

Neptunium hexafluoride was prepared by reacting neptunium oxide, obtained from Oak Ridge National Laboratory, with elemental fluorine at a temperature of 540°C using the fluorination system shown in figure B-2. The reaction tube consisted of a 1-in. O.D. nickel tube welded at both ends with a thermocouple well positioned directly above a nickel boat containing the oxide. The volatile NpF_6 formed was collected by passing the NpF_6-F_2 effluent stream through three cold traps arranged in series and cooled to -78°C using a carbon dioxide trichloro-trifluoroethane (R-113) slush. After collection in the cold traps, the NpF_6 was purified by trap-to-trap distillation under vacuum.

Preparation, collection, and purification of plutonium hexafluoride was conducted by a similar procedure except the starting material was PuF_4 which was obtained from Hanford Atomic Products Corporation, Richland, Washington.

The purity of the hexafluorides was checked by measurement of the vapor pressure at the ice point (0°C). The observed vapor pressures of UF_6, NpF_6, and PuF_6 are shown in table B-1 and compared with values given in the literature. The NpF_6 was stored as a solid while the PuF_6 was diluted with helium and stored as a gas in a prefluorinated nickel cylinder.

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*Hoke, Incorporated, Cresskill, New Jersey.

GLOVE · BOX

Figure B-1

VACUUM

N_2, F_2, or He

30" VAC.
TO 60 PSIG

UF$_6$ SOURCE

GAS PIPETTES

MIXING CYLINDER

He

0-20MM PBM

0-16 PSIA PBM

0-50MM PBM

SAMPLE CONNECTION

VAC.

PuF$_6$ CONTAINER

NpF$_6$ CONTAINER

PIPETTE SYSTEM

PBM
0-20MM

30" VAC
TO 60 PSIG

VAC.

COLD TRAPS

TUBE

F_2

T/C

FURNACE
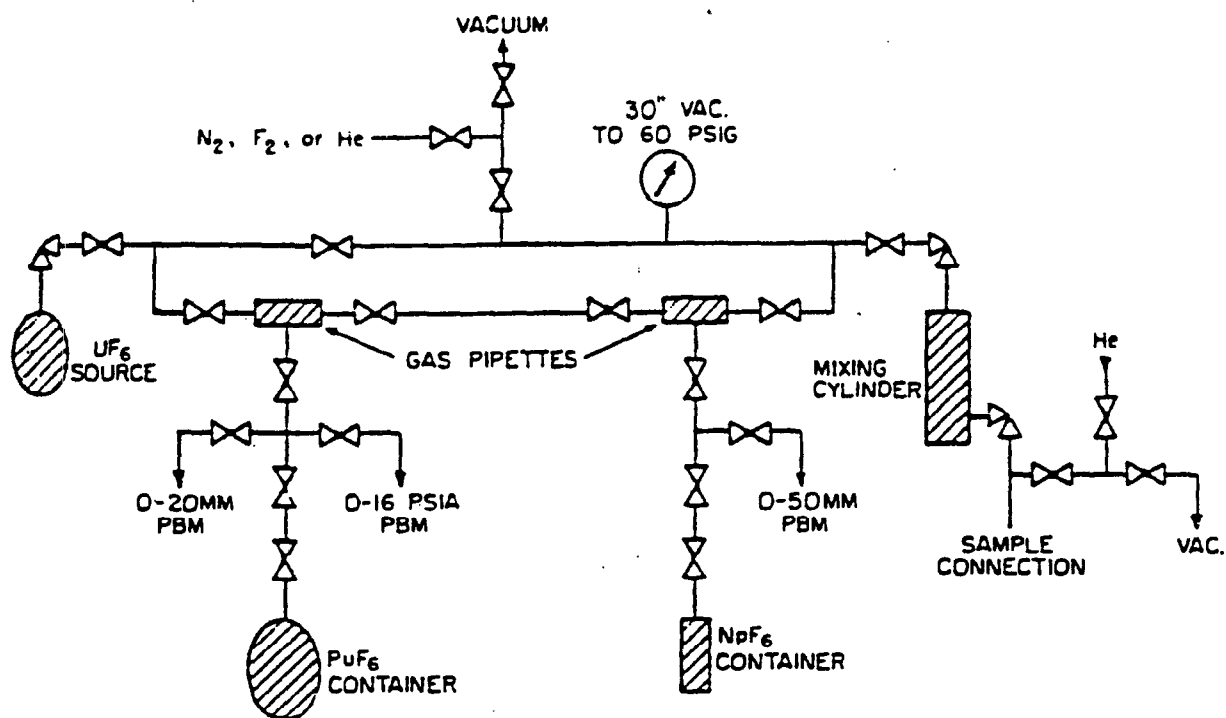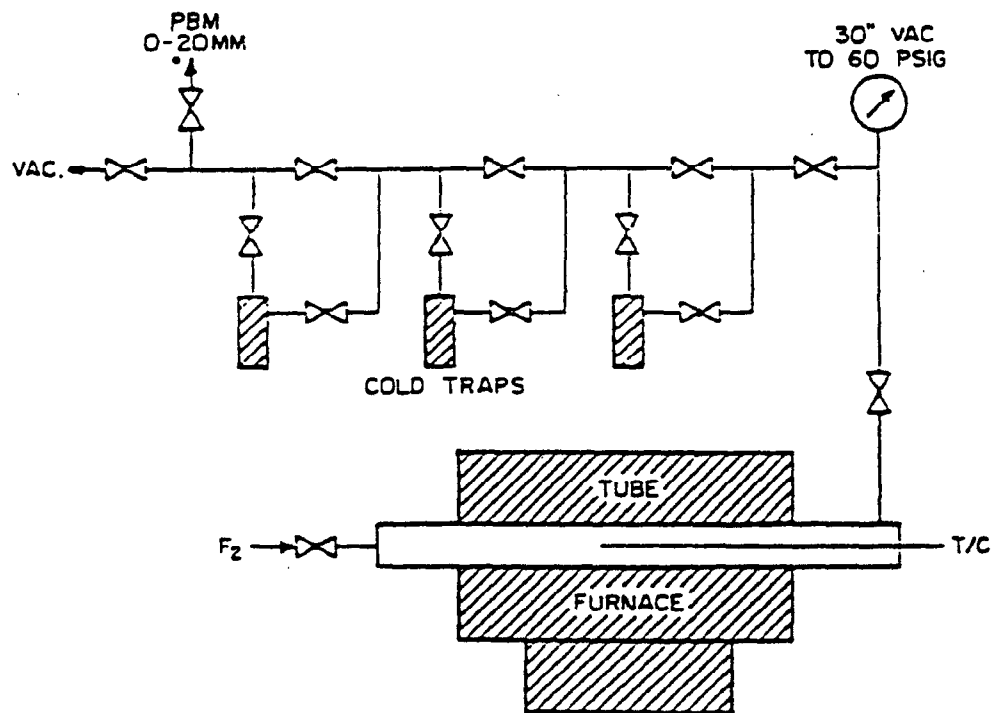
FLUORINATION SYSTEM

SCHEMATIC DIAGRAMS OF TWO SYSTEMS IN THE ALPHA BOX

FIGURE B-2

Table B-1

VAPOR PRESSURES OF NpF$_6$, PuF$_6$, AND UF$_6$ AT 0°C

Compound	Observed Pressure, mm Hg	Literature* Value, mm Hg
UF$_6$	18.0	17.5
NpF$_6$	20.6	20.8
PuF$_6$	17.5	17.6

*Weinstock, B., et al., *J. Inorg. Nucl. Chem.*, **11**, 104-114 (1959).

Neptunium tetrafluoride was prepared by the reduction of NpF$_6$ with elemental bromine as shown in the equation:

$$3 \; NpF_6 + Br_2 \rightarrow 3 \; NpF_4 + 2 \; BrF_3$$
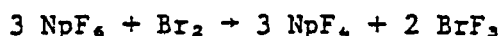
Neptunium hexafluoride was condensed into a fluorothene tube at -195°C and an excess of bromine condensed onto the NpF$_6$. The resulting mixture was slowly warmed to approximately 75°C. During this time the sample color changed to light brown as the bromine penetrated the solid and then to green, indicative of NpF$_4$. The product was purified by vaporization of the volatile fluorides and free bromine. Valence analysis characterized the sample as NpF$_4$.

Preparation of UF$_6$-NpF$_6$ and UF$_6$-PuF$_6$ Mixes

The initial UF$_6$-NpF$_6$ mix, designated Np-1, was prepared using the gas pipette system shown previously in figure B-2. A measured NpF$_6$ pressure was admitted to a known pipette volume and subsequently transferred from the pipette into the receiving cylinder. Uranium hexafluoride was then passed through the pipette and into the cylinder. PVT measurements were used to calculate the theoretical concentration of the mix. The Np-1 mix was used as a master mix for preparation of lower concentrations of UF$_6$-NpF$_6$ mixtures. A dilution technique was employed whereby three subsamples of UF$_6$-NpF$_6$ were removed from the master mix. Two of these were analyzed for neptunium and the third was vaporized into a cylinder and diluted with pure UF$_6$ to obtain the desired concentration. Analyses of wash solutions from the sampling tube and vaporization adaptor fitting allowed the necessary corrections to be made to compensate for the NpF$_6$ which decomposed on equipment surfaces during the transfer of the NpF$_6$ from the sampling tube to the cylinder.

The pipette system was also used to prepare the initial UF$_6$-PuF$_6$ mixture; however, the majority of the PuF$_6$ was reduced in the manifold lines due to the greater reactivity of the PuF$_6$. This method

was abandoned, and a dilution method was devised whereby a measured quantity of pure PuF₄ was collected in a fluorothene tube, vaporized into a cylinder, and diluted with UF₆ to obtain the desired concentration. Satisfactory results were obtained by this method.

Sample Handling

The sampling experiments are described in appendix C. While different techniques were attempted to obtain samples, the sample handling and analysis procedure was consistent with one exception. All samples were taken into a sample tube as shown in figure B-3. The tube shown was constructed of copper which is the preferred material. Tubes of similar design but made from fluorothene were also used. Under most circumstances these are satisfactory, but the fluorothene does absorb a small amount of activity which can introduce a bias in low activity samples. The bias can be either positive or negative depending on the contamination level and the sample tube history.

To prepare the sample for analysis, the sample tube was cooled in dry ice slush, the brass plug and flare nut removed, and the tube contents dissolved in a solution of 6 N nitric acid and 0.1 M aluminum nitrate. If the copper sample tube is used, it also dissolves in the hydrolysis solution. This causes no difficulty in the analysis and eliminates bias problems and tube cleaning which is an uncertain art at the low concentrations.

Neptunium and plutonium analysis was accomplished by first separating the neptunium and/or plutonium from the uranium by solvent extraction. The transuranic elements remain in the organic phase which is alpha counted to determine the amount present. The lower limit of neptunium detectability was 0.01 ppm on a uranium basis and 0.05 ppb for plutonium. All measurements above these lower limits of detectability are reported as positive values.

3/8" MALE BRASS PLUG

TEFLON GASKET

3/8" COPPER TUBE

SPUN BOTTOM

SOLDERED TIP

3/8" FEMALE FLARE
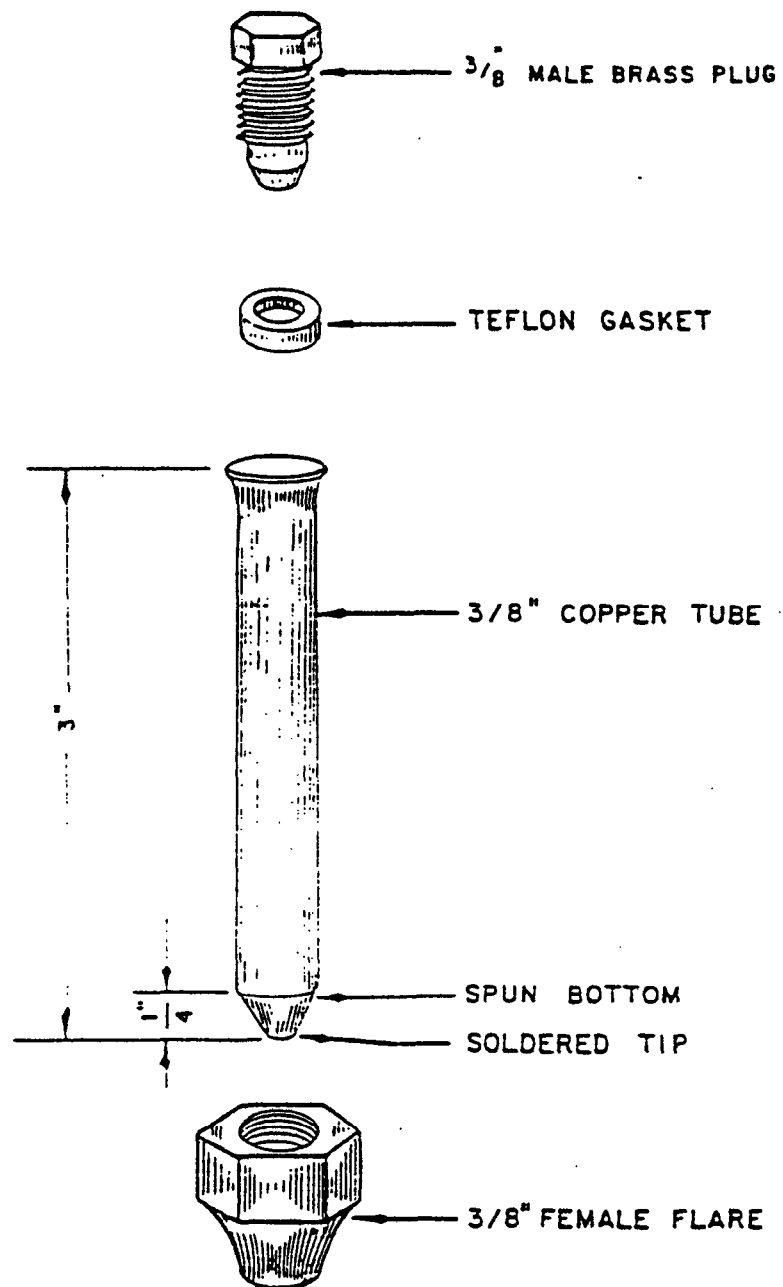
COPPER SAMPLING TUBE

FIGURE B-3

Appendix C

SAMPLING EXPERIMENTS

The primary goal of the initial experiments was to develop a sampling technique that could be applied to plant cylinders to obtain a representative sample of the material being fed to the cascade. To this end, a series of experiments was conducted using both nickel and steel equipment where it was intended to show that samples taken through a filter would predict the amount of transuranics that would be transferred by a simple vaporization process. Also, the tests were designed to show that unfiltered samples would be unsatisfactory. Only the latter goal was entirely achieved, but much information pertaining to the behavior of the transuranic elements in UF_6 was obtained, and a practical sampling method was developed which should serve the purpose of protecting the diffusion plant.

Initial sampling and vaporization studies were performed in nickel containment vessels. These cylinders were designed to safely contain one kilogram of UF_6. A 1/4-inch copper coil was soldered on the external surface of each cylinder to permit either steam heating or cooling by circulation of a refrigerant. Before use, the cylinders were thoroughly cleaned, dried, and pretreated with fluorine to form a protective nickel fluoride film to minimize reduction of NpF_6 and PuF_6 through contact with the nickel surface.

The general procedure which was followed in most of the sampling experiments is described below. A UF_6-NpF_6 or UF_6-PuF_6 mixture of the desired concentration was prepared in a cylinder by the dilution technique. The mixture was liquified and held at 100°C for approximately 24 hours with occasional shaking to ensure homogeneity. Ten or more liquid samples of approximately 5 grams each were removed for analysis. The remaining mixture was then totally vaporized into a second clean cylinder which was homogenized and sampled in a similar manner until all the remaining material was removed. Both containers and filters were washed with hydrolysis solution and all washings and solutions analyzed. Finally, a material balance was calculated for each mixture.

The early sampling and vaporization tests were in the nature of exploratory investigations to define the major problem areas of sampling low concentration mixtures of NpF_6 and PuF_6 in UF_6. Several things were apparent from these experiments. Some NpF_6 and PuF_6 was always reduced through reaction with container walls even though a protective nickel fluoride film had been predeposited on the metal surfaces. This partial reduction produced a two-phase system composed of soluble NpF_6 or PuF_6 and insoluble NpF_4 or PuF_4 which greatly complicated the problem of obtaining representative samples. The dilution method of producing low concentration mixes appeared to be a satisfactory technique for obtaining desired neptunium and plutonium levels provided allowance was made for some reduction and subsequent retention in the transfer system.

As a result of these experiments, it was concluded that in order to obtain reproducible results, even from these carefully prepared mixtures in clean stabilized systems, it would be necessary to filter the liquid samples being withdrawn to exclude particulate NpF_4 and/or PuF_4. A technique was employed whereby samples were passed through a micron-sized sintered metal filter prior to entering the sampling tube. Finally, since the plant cylinders are steel, a few vaporizations were done using steel cylinders rather than nickel. The results of these tests are given in tables C-1 and C-2.

Considering first the neptunium data (table C-1), several points should be noted. Mixtures prepared in nickel cylinders resulted in a concentration of 50 - 70% of the expected value. But if steel cylinders were used, the highest percentage obtained was only 25% in mixture 12. In the more dilute solutions, the yield was as low as 1% of the expected value. This is not unexpected since, as was noted in the development of the CoF_3 trap, both neptunium and plutonium hexafluoride are easily reduced. No specific analysis was made, but subsequent data convincingly indicates that nonvolatile tetrafluorides are formed. The mechanism likewise was not investigated, but it is presumed that the metallic walls of the cylinders and system are involved in the reduction. It may also be possible that UF_5 which would be present, particularly in the steel cylinders, could be involved in reducing the transuranics.

After preparing the mixtures and obtaining the liquid samples, the material remaining in the cylinder, representing approximately half of the original mixture, was vaporized into a second cylinder. In the early runs, 7 and 8 for instance, the material was vaporized directly, but in most later runs the gas stream was filtered prior to condensation in the second cylinder. The concentration in the second cylinder was then determined by hydrolyzing the entire cylinder contents and washing the cylinder with the nitric acid-aluminum nitrate solution. In the runs where the gas stream was not filtered, 7, 8, 9, 17, and 18, the neptunium concentrations were higher than determined by the original liquid samples. This means that there was a significant amount of carry-over of NpF_4 dust during the vaporization and indicates that regardless of other considerations the diffusion plant feed must be filtered. In all the cases where a filter was used, the neptunium concentration of the vaporized material was below that of the filtered liquid samples.

The fact that the filtered vaporized material always had a lower neptunium concentration than the original filtered samples was not expected; they should be the same provided no decomposition occurs during vaporization. As will be shown, NpF_4 is insoluble in UF_6; thus, the only neptunium being measured in the filtered liquid samples should be the soluble NpF_6. One possible explanation for this discrepancy could be that additional NpF_6 reduction occurs in the transfer lines and gas filter during the transfer. This happens to a limited degree, and some neptunium is found in the filter. However, based on the runs where a

Table C-1

NEPTUNIUM SAMPLING TESTS

Mix No.	1	10	8	7	14	9	15 (Blank)	23	19	13	12	11	17	21	18
Nominal Conc., ppm	300	300	3.0	1.7	0.17	0.15	0	27.5	24	16	15.7	13.4	9.2	4	0.44
Actual Conc., ppm															
By filtered liquid sample	193	196	1.84	0.87	0.12	0.093	0.033	0.27	2.21	3.47	3.96	2.16	0.36	0.018	0.04
By unfiltered liquid sample	166	193	-	-	-	-	-	-	-	-	3.10	3.53	-	1.57	-
Of vaporized material	194	-	1.94	1.63	0.06	0.23	0.07	-	1.19	3.41	0.27	0.30	0.86	-	0.14
Type Cylinder	Ni	Ni	Ni	Ni	Ni	Ni	Ni	Fe	Fe	Fe	Fe	Fe	Fe	Fe	Fe
Filter in Vapor Transfer Line	-	-	No	No	Yes	No	Yes	No	Yes	Yes	Yes	Yes	No	-	No
Material Balance, µg															
Added	-	-	855	543	38	39	0	-	6439	4312	4836	3910	2605	-	130
Removed:															
In samples & conditioning	-	-	253	105	25	12	10	-	248	366	212	162	62	-	5
In system washings	-	-	165	88	35	28	4	-	5760	3084	4359	3634	2724	-	98
In vaporized UF$_6$	-	-	274	174	7	34	9	-	108	542	39	29	173	-	16
Total	-	-	692	367	67	74	23	-	6115	3992	4610	3796	2959	-	119
Missing*	-	-	163	176	(29)	(35)	(23)	-	324	320	226	P2	(354)	-	11
Recovery, %	-	-	81	67	174	188	-	-	95	93	95	98	114	-	91
LF$_x$, Filtered Samples	28	17	0.28	0.27	0.11	0.041	-	0.11	0.44	0.75	10.5	2.78	0.33	-	0.05
LF$_x$, Unfiltered Samples	52	19	-	-	-	-	-	-	-	-	7.7	10.0	-	1.56	-

*Parentheses indicate amounts found above amounts added.

Table C-2

PLUTONIUM SAMPLING TESTS

	1	1-2	2	3	3-2	4	4-2	4-3	5
Nominal Conc., ppm	3.7	9.6	11.1	39	22	126	53	0.0038	115
Actual Conc., hrs/ppb	24/1.4	24/0.7	24/3.4	24/1.8*	24/0.6*	22/39,900			15/834
				24/2.1**	24/26 **	43/36,100			17/65
						⊢→→→→⊢→ 23/5040			19/67
						93/11.7			36/3.9
						⊢→→→→ 49/5.2			30/11
						54/0.4			40/5.4
									42/2.7
									63/0.4
									65/0.2
In Vaporized UF₆, ppb	–	9.1	2.8	–				80	
Material Balance, μg									
Added	–	4476	3370	24784				34200	
Removed:									
In samples & conditioning	–	0.4	<1	2				5510	
In system washing	–	81.7	721	17986				18870	
In vaporized UF₆	–	2.5	<1	9				20	
Total	–	84.7	722	17997				24400	
Missing	–	4391.0	2648	6787				9800	
Recovery, %	–	2	21	73				71	

*Fluorothene sample tubes.
**Cu sample tubes.

filter was not used and high neptunium concentrations were found in the vaporized UF_6, it is concluded that most of the neptunium found in the filter was dust carry-over, i.e., NpF_6. While some reduction probably occurs, this does not appear to be a likely explanation of the problem.

Another possibility lies in the relation between the insoluble NpF_4 particle size and the pore size of the filter. A two-micron filter was chosen, more or less arbitrarily, for both the liquid sample filtering and for gas stream filtering during vaporization. The particle size of the NpF_4 could be smaller than two microns. Considering the possible reduction mechanisms, cylinder walls, or UF_3, it would be likely that any NpF_6 reduced by UF_3 would be in the form of very small particles considering the concentration of the reacting materials. However, there is at least some data, mixture 21, where almost no neptunium was found in the filtered UF_6. Obviously, little or no NpF_4 passed through the filter in this case.

The most convincing evidence that the filter is effectively filtering out the solids lies in the precision of the data obtained with a filter compared to that obtained without the filter. Table C-3 summarizes the precision of all the sampling data.

Table C-3

NEPTUNIUM DATA PRECISION
FILTERED VERSUS UNFILTERED SAMPLES

Neptunium Conc., ppm:		$\bar{X} \pm \%LE_{\bar{X}}$				
		< 1		1-10		> 10
Filtered Samples *	(21)	0.02±128	(8)	1.84± 15	(1)	193±15
	(18)	0.04±125	(11)	2.16±129	(10)	196± 9
	(9)	0.09± 44	(19)	2.21± 20		
	(14)	0.12± 92	(13)	3.47± 22		
	(23)	0.27± 41	(12)	3.96±265		
	(17)	0.36± 92				
	(7)	0.87± 31				
Average:		± 79		± 90		± 12
Unfiltered Samples	(21)	1.57±100	(12)	3.10±248	(1)	166±24
			(11)	3.53±282	(10)	193±10
					(1)	194±32
Average:		±100		±265		± 22

*Parentheses indicate mixture number.

One would expect that the scatter of the sample results would increase as the concentration decreases for reasons such as the increasing ease of contamination and the decreasing counting precision at lower counting rates. This is seen in the filtered samples where the average limit of error increases from 12% to 80-90% at the lower concentrations. If

one were to omit mixture 12, which appears to be out of line, one then would see the expected progressive increase in LE at decreasing concentration.

In the unfiltered samples, in addition to the contamination and counting problems mentioned above, one has to expect more variation because of a probable unhomogeneous mixture. This was reflected in the data where the limit of error was 100-300% at the lower concentration levels. At the 200 ppm level the influence of the filter was much less, but still the filtered samples were more precise.

While considering precision, a few general observations might help to place the problem in perspective. In comparison to much laboratory data, the precisions obtained do not appear to be very satisfactory, and this in fact did result in many problems in interpreting the data. The foremost problem was contamination which was very difficult to control at these low levels. Consider for a moment that most of this work was done in a glove box which also contained relatively large quantities of the volatile pure neptunium and plutonium compounds, and one can perhaps realize the difficulties faced. Also, it was increasingly realized during the studies that every piece of equipment, be it manifold, valve, filter, or sample tube, was apt to either add to or subtract somewhat from the neptunium or plutonium inventory depending upon its previous exposure history. For example, the blank run 15 (table C-1) shows quite well where the excess neptunium came from that was found in runs 9 and 14. While the majority came from the sample tubes, some was also found in washings from various parts of the system.

The most convincing evidence that the sampling data obtained were reliable and bias free, in spite of the problems faced, lies in the material balances obtained for most of the mixtures. Mixes 1 and 10 were the base mixtures which were diluted to make up the remaining mixtures. Mixtures 21 and 23 were used for special tests and no balances were obtained. Where balances are given it is believed that the recovery should be considered highly satisfactory considering the circumstances.

Returning to the original goal of this part of the studies, that of the development of a sampling program that would obtain samples which would represent the material being fed to the diffusion plant, it is believed that insofar as neptunium is concerned this goal has been substantially achieved. Assuming that the feed stream will be filtered, which these studies indicate should be done, then the filtered liquid samples will give the best representation found of the amount of neptunium that will be fed to the diffusion plant. One can say with confidence that when particulates are controlled the value obtained will not be exceeded. There is some indication that the samples will indicate more neptunium being fed than will be the actual case, but it is at best tenuous to compare the laboratory vaporization system to the considerably different plant equipment.

Considering the very similar chemistry, the method developed for obtaining the neptunium samples would be expected to be satisfactory for plutonium. Nevertheless, a few plutonium mixtures were made up to obtain

experience in the properties of the mixtures and to confirm the sampling procedure. The results have been shown in table C-2, and there were some significant differences between the properties of plutonium and neptunium mixtures.

The most pronounced difference was in the stability of the mixtures. Whereas the high level neptunium mixtures, 1 and 10, were kept for months with little change, the plutonium in the mixtures was reduced very rapidly. For example, the first four mixtures prepared were supposed to contain from 4 to 40 ppm plutonium, but after 24 hours homogenization time the highest concentration found was only 3.4 ppb. These and all other plutonium mixtures were made up in well conditioned nickel cylinders, but no success was achieved in preparing plutonium mixtures until those containing more than 100 ppm plutonium were attempted in mixtures 4 and 5. Even in these cases the reduction was essentially complete after a few days.

All samples were taken through filters, and considering the low level results it is clear that the filters were effective in filtering out the reduced plutonium. The accuracy and precision of the samples was a bit more difficult to establish than was the case with neptunium because of the extreme reactivity and because contamination was even a more difficult problem at the parts-per-billion level. Material balances were attempted with some success, but since almost none of the plutonium was soluble these yielded little positive information as to the accuracy of the samples. Mixture 4 which was diluted twice (mixtures 4-2 and 4-3) provides the only information on accuracy in that the initial samples did approximate the calculated concentrations. In mixture 4 the 22-hour sample was 39.9 ppm versus 126 calculated while for 4-3 the measured value was 5.2 ppb versus 3.8.

Data on sampling precision are given in table C-4. In the 5 - 40 ppm range the limit of error (95% confidence) of a single determination is about 17% while at the 1-25 ppb level the precision is about 125%. These values are similar to those found with neptunium at comparable count levels.

Considering the data, the properties of the two compounds in question, and the goals of the program, it is concluded that the method of taking liquid samples through a 2-micron filter is a satisfactory method for estimating the amount of neptunium and plutonium that would be fed to the diffusion plant, assuming that the material will be filtered prior to introduction to the plant. Any error will be on the conservative side in that the amount of impurities that would be estimated from these samples will probably be in excess of that actually fed.

A simple vaporization through a filter apparently results in some reduction of the neptunium concentration but not sufficient to be useful. The reason for the reduction is not clear, and the reaction does not appear to be sufficiently controllable to be useful as a technique for obtaining decontamination with large cylinders and plant systems. The data, table C-5, are quite scattered, but since it is believed that no practical use could be made of this phenomenon, no attempt was made to improve the data.

Table C-4

PLUTONIUM SAMPLING PRECISION

Plutonium Conc., ppm	ppb	LE_x, %
5.0		18
36.1		16
39.9		18
	Av.	<u>17</u>
	0.22	73
	0.26	123
	0.36	142
	0.59	48
	0.69	88
	1.4	66
	1.8	129
	2.1	121
	3.4	175
	3.8	116
	5.2	189
	11.7	80
	25.6	262
	Av.	<u>124</u>

## Table C-5

NEPTUNIUM DECONTAMINATION FACTORS
ACROSS VAPORIZATION STEP

Mixture	Neptunium Conc., ppm Pre-Vaporization*	Post-Vaporization*	DF
14	0.12	0.06	2.0
19	2.21	1.19	1.9
13	3.47	3.41	1.0
12	3.96	0.27	15
11	2.16	0.30	7

*Mixtures were vaporized through a sintered metal filter.

The filters through which the samples were taken were obtained from Mott Metallurgical Company and were designated as 2-micron size filtration grade. Figure C-1.
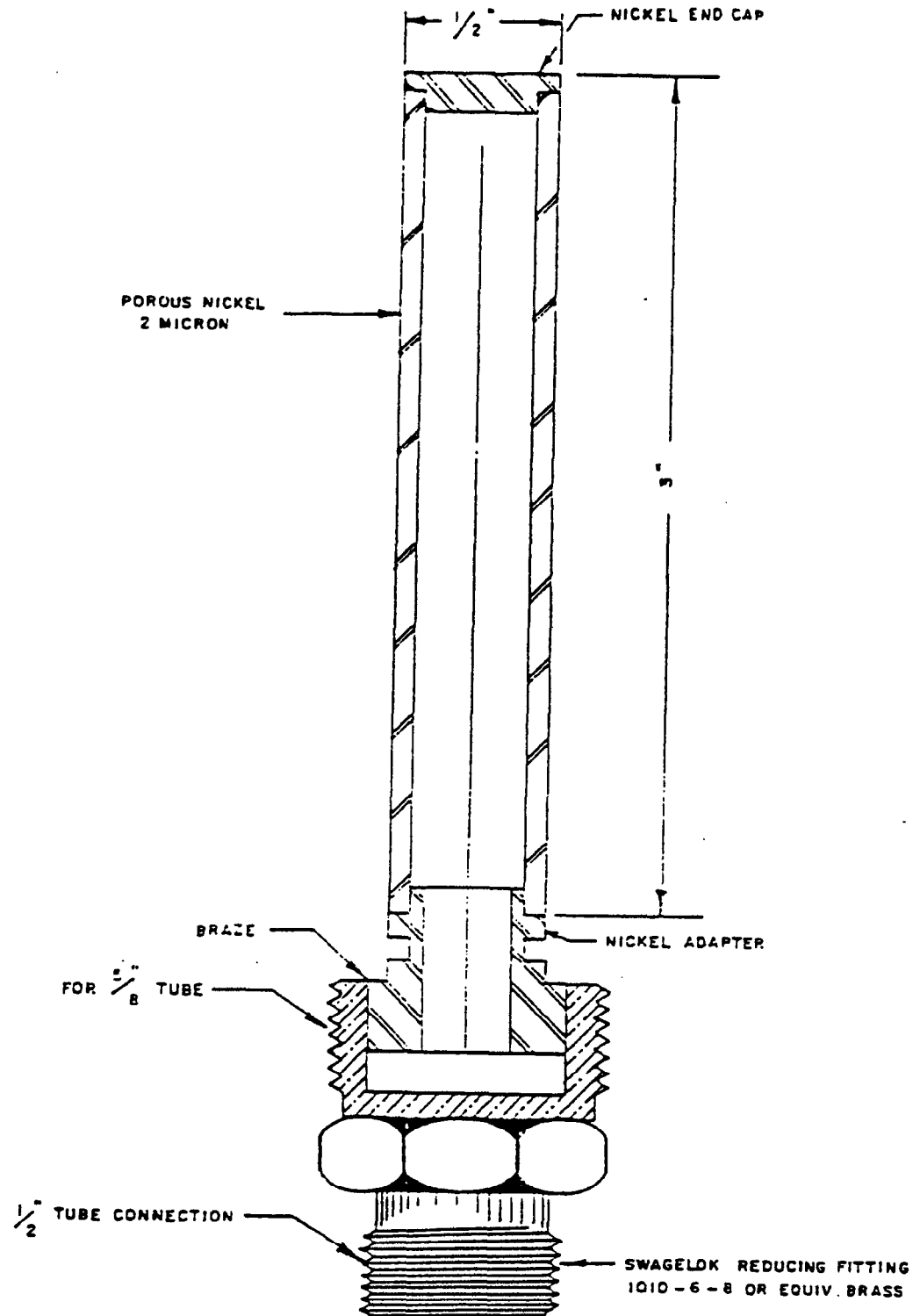
UF₆ IN-LINE FILTER

FIGURE C-I

Appendix D

SOLUBILITY OF NpF$_4$ AND PuF$_4$ IN UF$_6$

One objective of the sampling studies was the development of a method for predicting the volatile Np(VI) and Pu(VI) contained in a cylinder. Studies had confirmed that the method of filtering samples was satisfactory for precluding the particulate Np(IV) and Pu(IV) from samples. Also these studies had indicated that the solubilities of the tetravalent fluorides was low, but the extent of their solubility in liquid UF$_6$ had not been determined. Studies were conducted to investigate this area.

Two mixtures were prepared, the first containing 200 µg of NpF$_4$ per gram of UF$_6$ (200 ppm) and the second with 7.3 µg of PuF$_4$ per gram of UF$_6$ (7.3 ppm). The mixtures in nickel cylinders were heated to liquify the UF$_6$, agitated, and allowed to stand a minimum of 24 hours. Filtered liquid samples were taken, using the established techniques, and then analyzed for neptunium and plutonium. The results of the individual analyses are given in table D-1. Over the temperature range investigated, 80-120°C, no temperature effect was seen. The solubility on a metal basis, i.e., Np/U or Pu/U, was less than 18 ppb for NpF$_4$ and 4 ppb for PuF$_4$. At these extremely low levels, the experimental techniques, particularly from contamination, preclude obtaining precise data, but the results obtained are considered quite consistent. Any bias would be expected to be positive. The field test of the sampling procedure described next provides additional data which indicates the PuF$_4$ solubility is considerably less than 4 ppb.

Table D-1

SOLUBILITY OF NpF$_4$ and PuF$_4$ IN UF$_6$

	NpF$_4$, ppb *			PuF$_4$, ppb *		
	90°C	105°C	120°C	80°C	95°C	110°C
	10	30	30	6.9	1.9	3.7
	10	30	20	3.7	7.6	3.8
	<10	40	20	2.4	5.7	2.7
	10	<10	<10	3.0	4.4	2.1
	20	10	<10	-	-	3.5
	10	10	<10			
	20	20	<10			
	10	20	<10			
	-	20	<10			
	-	<10	<10			
Av.	13	20	14	4.0	4.9	3.2

*Np/U or Pu/U basis.

The data from the solubility studies provides additional evidence that the sampling procedure developed is adequate for sampling a two-phase system. The upper limit for the solubility of NpF_6 and PuF_6 will not significantly bias the sampling of minutely contaminated material, and the results can be considered as representative of only the volatile NpF_6 and PuF_6 contained in the UF_6.

FIELD TEST OF THE SAMPLING PROCEDURE

A special test, designed to evaluate under field conditions the transuranic sampling procedure, was conducted using a 2.5-ton cylinder (No. D-45525) of UF_6 containing neptunium and plutonium from reprocessed foreign reactor fuels. A sampling buggy was converted to a transuranic sampling station and was constructed to be similar to the anticipated permanent installation. A schematic drawing of the system is shown in figure E-1.

The 2.5-ton cylinder was heated in an autoclave at approximately 100°C for approximately 14 hours. The sampling system was then conditioned by withdrawing seven samples through the pipet and lines into the dump container. A series of 13 filtered samples was taken from the cylinder followed by 10 unfiltered samples. The cylinder was then heated for an additional 24 hours at 93 ± 2°C and another series of 10 unfiltered samples was taken followed by 10 filtered samples. The samples were taken in copper tubes, and each tube and its contents were put in solution with 6 $\underline{M}$ HNO_3 - 0.1 $\underline{M}$ $Al(NO_3)_3$.
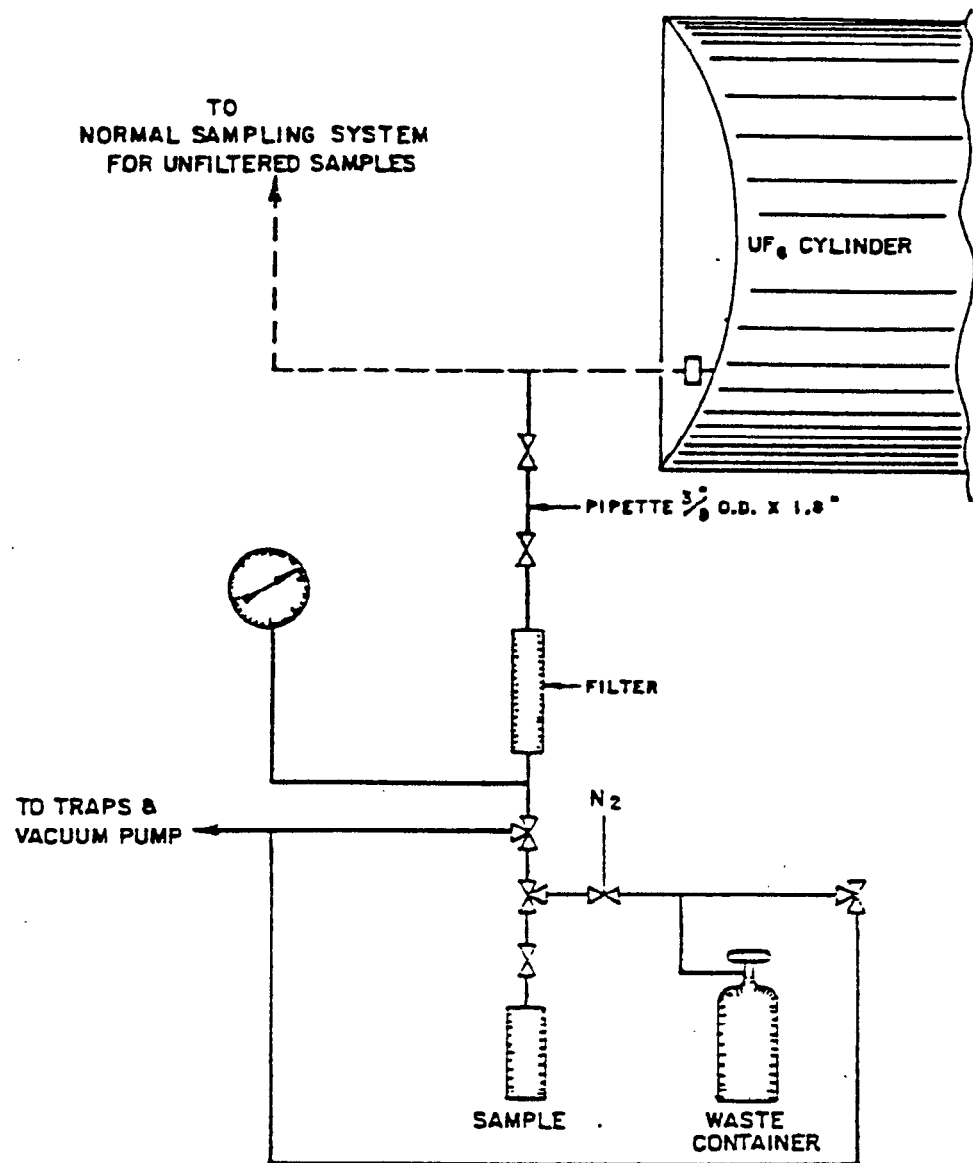
It was anticipated that each sample would be approximately 10 grams; however, early samples were more in the neighborhood of 1 to 3 grams. The system was obviously not completely conditioned as may be seen by the data in table E-1. After the first 10 samples had been taken, the pipet temperature was lowered slightly to ensure that the contents would be liquid and the sample size increased accordingly. This experience points out the necessity for withdrawing enough material through the sampling system to thoroughly condition the surfaces or low results will be obtained. The complete set of sample data is summarized in table E-1.

Table E-1

SAMPLING SUMMARY

Sample Set	Neptunium Conc., ppb		Plutonium Conc., ppb	
	Filtered	Unfiltered	Filtered	Unfiltered
1	10*	61±25	0.084*	35.6±17.4
2	17	101±57	0.61±0.29	31.7±16.5

*System not stabilized

TO
NORMAL SAMPLING SYSTEM
FOR UNFILTERED SAMPLES

UF$_6$ CYLINDER

PIPETTE $\frac{3}{8}$ O.D. X 1.8"

FILTER

TO TRAPS &
VACUUM PUMP

N$_2$

SAMPLE

WASTE
CONTAINER

NOTE

SOLID LINE ARE NICKEL

PLANT CYLINDER SAMPLING SYSTEM

FIGURE E-1

The plutonium data in the table were converted from the counting results on the basis that 40% of the alpha activity was due to ^{238}Pu and 60% to ^{239}Pu. On a weight basis this means that approximately 99.8% of the plutonium was the 239 isotope.

While these data may not be exactly typical in that this was a small cylinder (2.5 ton) which had been liquified and sampled at least once previously, the data are quite useful and generally support the original laboratory conclusions. First, there is a large difference between the filtered and unfiltered data. At least 83% of the neptunium was reduced, assuming the true value is near the less than 17 ppb value reported for the second set of data. A different interpretation of the 17 ppb neptunium value is that there is no NpF_6 present and the measured value represents the solubility of NpF_4. Using this route, one could also perhaps include the less than 10 ppb value determined from the first set of samples. Either explanation is reasonable and is not inconsistent with previous data which indicated a solubility of less than 18 ppb (appendix D).

Considering the plutonium data in the same manner, one would conclude that at least 98% of the PuF_6 was reduced, or that the solubility of PuF_4 was 0.61 ppb, or less than 0.08 ppb as determined from the set 1 samples. These values compare with the PuF_4 solubility value determined in the laboratory of 4 ppb. The fact that essentially all of the PuF_6 was reduced agrees with all the laboratory data, but there is no way to distinguish between 98% reduction which is what the second set of samples indicate or 100% which would be the case if the solubility of PuF_4 is 0.61 ppb. Having experienced the contamination problems that were encountered in this program from the beginning, one is most prone to accept the lowest of any possible values as the most likely to be correct. Using this reasoning leads one to accept a value of less than 0.08 ppb for the solubility of PuF_4 in UF_6.

The solubility value of 0.08 ppb for PuF_4 in UF_6 is approximately equivalent to 11 α dpm/gU due to ^{239}Pu. While at these low levels it is sometimes difficult to be explicit about data interpretation, it can be fairly concluded that the sampling procedure was successful and that it has been amply demonstrated the filtered samples provide the best representation of the composition of the UF_6 being vaporized from a cylinder. At the same time this work shows the necessity for attention to detail and care that is necessary for obtaining good, representative samples.